
**COLLECTED
SCIENTIFIC PAPERS OF
MEGHNAD SAHA**



COLLECTED SCIENTIFIC PAPERS OF MEGHNAD SAHA • COLLECTED SCIENTIFIC PAPERS OF MEGHNAD SAHA

COLLECTED SCIENTIFIC PAPERS OF MEGHNAD SAHA

COLLECTED SCIENTIFIC PAPERS OF MEGHNAD SAHA • COLLECTED SCIENTIFIC PAPERS OF MEGHNAD SAHA



COLLECTED SCIENTIFIC PAPERS OF MEGHNAD SAHA

**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
GOVERNMENT OF INDIA
NEW DELHI
1969**

PRICE: Rs. 60.00 Sh. 120 \$ 18.00

**COMPILED AND EDITED BY
SANTIMAY CHATTERJEE
SAHA INSTITUTE OF NUCLEAR PHYSICS
92, ACHARYA PRAFULLA CHANDRA ROAD
CALCUTTA-9, INDIA**

**COVER PAGE DESIGNED BY
SHYAMAL NANDY
RANJAN KUNDU
DIAGRAMS BY
RANJAN KUNDU**

**PRINTED BY
S. N. GUHA RAY
AT
SREE SARASWATY PRESS LTD.
32, ACHARYA PRAFULLA CHANDRA ROAD
CALCUTTA-9**



FOREWORD

Dr. Meghnad Saha, D.Sc., F.N.I., F.R.S. was born at Sheoratali, a village near Dacca (now in East Pakistan) on October 6, 1893. His childhood was spent in that obscure village and his parents were not in a position to support his education even in school. At every stage of his educational career Meghnad had to win merit scholarships to meet the expenses for his own education at school, college and University. He joined the Presidency College, Calcutta as a student in the B.Sc. class in 1911.

The first occasion I came across Meghnad Saha without knowing his identity was in April, 1913, when I examined a batch of B.Sc. candidates in pass practical physics in the Scottish Churches College. Later I was told by Satyendranath Bose that he with Meghnad Saha, Jnan Chandra Ghosh, Jnanendra-nath Mukherjee were amongst the candidates I had examined.

In 1917 while interned in Germany I was able to publish a short note in the *Physi-calische Zeitschrift* on photographs of recoil tracks of hydrogen atom in a Wilson Expansion Chamber filled with hydrogen when bombarded with alpha particles from Polonium. I was able to send a few reprints to Calcutta. Through the kindness of Dr. P. C. Ray one of them reached Meghnad Saha who translated it from German and sent a copy of the same to my mother. This was the first intimation I got of Meghnad Saha who could read and translate from German. Later on after my return to Calcutta in July 1919 I received a copy of Saha and Bose's translation of some of Einstein's papers on Relativity.

I joined the Physics Department of the University College of Science in 1919 after my enforced five years' stay in Berlin. Two of my young colleagues in the Physics Department, Meghnad Saha and S. N. Bose, had been starved of information about the advancement in Physics which took place in Germany, specially in Berlin. At that time were congregated in Berlin scientists like Planck, Einstein, Warburg, Max Born, Walter Nernst, promulgators of Quantum and Relativity theories and their further theoretical development and experimental verification.

I remember the characteristics of my two colleagues which illustrated their different approach towards scientific research. I gave S. N. Bose two books written by Planck, *Thermodynamik* and *Warmestrahlung*, to read, as they were not available then in this country. S. N. Bose appreciated very much the logical way in which Planck deduced the whole of Thermodynamics from a limited number of postulates. On the other hand, Planck's deduction of his famous formula on the spectral distribution of energy in black body radiation was based mainly on classical Electromagnetism and Thermodynamics to which a single quantum postulate had been added. S. N. Bose noted the inner inconsistency in Planck's exposition and missed in it the clear logical formulation which characterized Planck's *Thermo-dynamik*. This intellectual dissatisfaction with Planck's deduction of his radiation formula led, I believe, to Bose's deduction on a combinatorial basis of Planck's formula in 1925.

Meghnad Saha's approach was more direct; he wanted to learn from me the latest advances on the frontiers of research in Physics in relation to Quantum Physics and Thermodynamics. From time

to time he discussed with me the theory of thermal ionization of gases and its application to the interpretation of stellar spectra. Saha was awarded the D.Sc. degree of the Calcutta University in 1919. He was also a recipient of the Premchand Roychand Studentship of the Calcutta University. Next year in 1920, as an examiner of Griffith Memorial Prize essays, for which the candidates had to give a *nom-de-plume*, I came across amongst other papers one by Heliophilus on 'Origin of lines in stellar spectra'. As the paper was so outstanding compared to other essays submitted for the prize, there was no hesitation in recommending it for the award of the Griffith Memorial Prize. Saha's paper published in the Proceedings of the Royal Society in 1920 secured immediate recognition. Rosseland, in evaluating the contribution of Saha to Astrophysics, remarked: 'The impetus given to Astrophysics by Saha can scarcely be overestimated, as nearly all the later progress in this field has been influenced by it and much of the subsequent work has been refinement to Saha's theory.' In 1920 Saha went for one year's study to England and Germany; after his return, from 1921 to 1923, Saha was Khaira Professor of Physics in the University College of Science, Calcutta. During this period he discussed with us the possibility of carrying out laboratory experiments for verification of his theory. The resources at our disposal were not adequate enough. Later on, towards the end of his period of stay at Allahabad, Saha received a munificent grant from the Royal Society of London by means of which his students in Allahabad were able to verify some of his predictions. Saha would have been very pleased to follow the results of recent magneto-hydrodynamic experiments in which a gas, raised to a high temperature and seeded with volatile compounds of an alkali metal and made to flow with high velocity across a transverse magnetic field, delivers an electric current between insulated electrodes placed transverse to the magnetic field and the direction of flow of the gas.

The thermal ionization in gas and its application to the elucidation of the stellar spectra, which he published in 1920 when only 27 years of age, is the most outstanding and original work on which Saha's fame as a physicist will rest. Saha with his students published a number of other important theoretical papers in Spectroscopy, on the propagation and reflection of electric waves in the upper atmosphere; but these are not of the same importance as his series of papers on thermal ionization in gases. During his 15 years' stay in Allahabad (1923-38) Saha had built up an important school of theoretical and experimental Physics; D. S. Kothari, R. C. Majumdar, P. K. Kichlu, G. R. Toshniwal, B. N. Srivastava, A. N. Tandon and many others belonged to this group.

During the period 1923 to 1930 my contact with Saha was infrequent. After the Banaras Science Congress in 1925 Saha and N. R. Dhar persuaded us to go to Allahabad where I stayed with my friend Prof. A. C. Banerjee. I spent most of my days in Saha's laboratory delivering some lectures and attending colloquium. On a subsequent occasion I went to Allahabad to conduct practical examination and stayed in Saha's commodious house where he later entertained Sommerfeld and Eddington, and met some of the scholars who were staying with Saha. My memory also goes back to the Science Congress session in 1926 in Bombay when Saha was the President of the Physics section. In his Presidential address Saha gave a very comprehensive review of the Theory of Thermal Ionisation and the service it had rendered in increasing our knowledge of the sun and the stars. He showed how as in the past so in the present age, a renaissance in physics and mathematics has been marked by an outburst of activity in astronomy.

We again met during the Science Congress session at Lahore in 1927 where I was the President of the Physics section. Amongst the senior scientists present were S. N. Bose, M. N. Saha and Prof. A. H. Compton. The year 1927 proved to be an eventful one for us. Early in the year I received an invitation from the Volta Centenary Celebration Committee to attend an International Congress on Physics to be held at Como, Italy during September, 1927. Meghnad Saha had also received a similar invitation to attend the Congress at Como. In addition he received the happy news of his election to the Fellowship of the Royal Society. When Saha came to Calcutta on his way to Europe the Physics Department arranged a reception in his honour. It was arranged that Saha and myself should meet in Como and stay in the same hotel. It happened to be the Hotel St. Gothard, where Prof. Eddington also happened to be a guest.

On November 23, 1937 Jagadish Chandra Bose passed away. The following April I joined as Director, Bose Institute, resigning my post as the Palit Professor of Physics in the Calcutta University. In the vacancy thus created Meghnad Saha was appointed the Palit Professor. The city of Calcutta provided him a larger sphere of work and offered him opportunities a provincial town like Allahabad had

lacked. About the end of 1946 I was present at a dinner given by Saha for Jawaharlal Nehru. The company included some of the Calcutta physicists like P. C. Mahalanobis, S. K. Mitra, myself and others. Saha, at that time was deeply concerned about the problems of national planning and it was at this party that I became aware of his involvement in the issue. Saha became an important member of the National Planning Committee of the Indian National Congress constituted by Netaji Subhas Chandra Bose with Jawaharlal Nehru as Chairman.

Up to 1930 Saha was entirely engrossed in teaching and research in Science. In 1952, when he entered Parliament, Saha explained how the new phase of his activities which dealt more with organization of research and the application of Science to national development problems began. 'Scientists are often accused of living in an Ivory Tower and not troubling their mind about realities; apart from my association with the political movement of my juvenile years, I lived in the Ivory Tower till 1930.'

These extramural activities, which gradually occupied an increasing share in Saha's activities, can be divided into two groups. In the first could be placed those activities which dealt mainly with extending the scope of scientific research in the country and the support of research by establishing new laboratories for special type of research, by reorganization and extension of scientific research in already well-established institutions, by establishing academies of science, and journals for the popularization of science and its application to national problems.

Saha realized in 1930 that for communication of results of scientific research and for their discussions more academies of science and specialist societies were necessary.

In 1931 on his initiative, the U.P. Academy of Science was founded whose name was later changed to the National Academy of Science. His expectation that this body would serve as an all-India academy did not materialize when another body, the Indian Academy of Science, was started in Bangalore.

An influential group of Indian scientists felt at this time that these regional bodies could not serve the function of an all-India organization. In his presidential address before the Indian Science Congress held at Poona in 1934, Saha strongly stressed the need for such a body. It led to the formation of an Academy of Science Committee with Saha and S. P. Agharkar as Secretaries. As a result of their deliberations the National Institute of Sciences of India was inaugurated in Calcutta and started functioning from January 1935. In 1945 the headquarters of the Institute were removed to Delhi. Between 1933 and 1935 Saha was responsible for the foundation of two other scientific organizations in Calcutta, the Indian Physical Society in 1933 and the Indian Science News Association in 1935.

During the period 1935-53 Saha used *Science and Culture*, the journal of the Science News Association, as the vehicle for propagating his ideas on the application of Science to national development.

I recall Saha's achievement in providing Calcutta with two well-equipped institutions for research in physicochemical sciences and in nuclear physics.

The original buildings of the Indian Association for the Cultivation of Science, where Raman and Krishnan with their research students did some very outstanding work—for which Raman was awarded a Nobel Prize and Krishnan elected Fellow of the Royal Society—proved inadequate for further laboratory extension. In 1944, mainly through Saha's efforts, the Association for the Cultivation of Science was provided with about 10 acres of land at Jadavpur on which a well-equipped laboratory for physical and chemical research has been erected. Through Saha's efforts mainly, the Association is receiving substantial grants from the Ministry of Scientific Research. As usual for a developing institution, the financial needs of the Institute have outstripped its present grants.

Soon after joining the Calcutta University as Palit Professor in 1938, Saha recognized the importance of the recently discovered nuclear fission of uranium by Hahn for research in nuclear physics and for the utilization of nuclear energy for industrial purposes. He introduced nuclear physics as a special subject in the M.Sc. syllabus and attempted to build up a special laboratory for nuclear physics. His single-handed efforts to establish a separate institute for nuclear physics in the grounds of the Science College led to the foundation stone of the Institute being laid by the late Syamaprosad Mookherjee in 1948 and the opening of the Institute by Mme. Joliot Curie in 1951.

During the period when Saha was establishing his Institute, the late H. J. Bhabha, between 1946 and 1948, succeeded in converting the existing Atomic Energy Committee to the Atomic Energy Commission, of which he became the Chairman. There was a tendency for the Commission to restrict the main developments of atomic energy to Bombay. It was an achievement of Saha to have secured recognition from the Commission of the Nuclear Physics Institute, Calcutta, and the sanction of a grant

amounting to about Rs. 50 lakhs for the Second Five-Year Plan period (1955-60). The grant has since been considerably increased. But for the Saha Institute of Nuclear Physics, Calcutta would have been deprived of all facilities for modern atomic and nuclear physics research. The Institute has still to build a modern atomic accelerator for the eastern region.

THE SECOND GROUP of activities in which Saha was engaged was concerned with the application of science and scientific methods to solution of problems of economic development of the country. This type of activities requires the co-operation of many types of abilities and experience; giving effect to such constructive proposals could only be possible through State efforts either during periods when a leader enjoying the confidence of the people became the head of Government or when a powerful group controlled the State machinery. Due to the complexity of the problems and our want of experience in dealing with them, at no stage has there been a complete diagnosis of the problems. We find that even now we are still grappling with their solution handicapped by lack of complete data, by wishful thinking and a certain amount of hesitation in decision-making.

Saha's importance lies in his being aware of such problems earlier than others, in his capacity for rapid mastery of the essentials of the problems, his matchless publicity campaign focusing public attention to them, putting forward some concrete solutions, and in severely criticising Government plans when necessary. It is, however, one thing to put forward a solution of a complex problem based upon available, generally incomplete, data and another thing to come to close grips with the problem, to realize its complexity and to try and evolve alternate pathways for its solution.

Some of the problems, attention to which was first drawn by Saha who also proposed their solutions are;

- (i) Organisation of scientific and industrial research
- (ii) Atomic energy and its industrial use
- (iii) River Valley development projects
- (iv) Planning the national economy
- (v) Reform of the Indian Calender

Saha has written many important original articles on these subjects over a period of thirty years and I hope some day a collection of those articles would be available in print.

As a member of the Parliament his contribution was substantial in evolving policies on education, scientific research and many other aspects of public life.

During the January of 1956 Saha was not keeping good health but in spite of friendly warning of his physician he continued to work with unabated determination. On February 16, 1956 while walking towards the office of the Planning Commission, Saha was seen to trip and fall down—he was recognised and taken immediately to a hospital; but he did not recover.

I have not tried to summarise the papers presented in this collection. Dr. D. S. Kothari has given a resume of Saha's work in his obituary note on Meghnad Saha in the Biographical Memoirs of Fellows of the Royal Society of London, 1959. It will be apparent to the readers of this volume that Meghnad Saha had worked on various fields in Physics though his name will always be remembered for his theory of thermal ionisation and its application to the interpretation of stellar spectra in terms of the physical conditions prevailing in the stellar atmospheres. Saha has also written a large number of review articles and two text books. The "Treatise on Heat" by Saha and Srivastava is still considered as a standard book all over the world. Saha also delivered a large number of addresses in scientific societies and some of these addresses were very important and had started new chains of thought. A collection of these addresses should also be published.

The Collected Scientific Papers of Meghnad Saha should have been published long ago. Professor Santimay Chatterjee deserves our thanks for fulfilling this long-felt need.

October 6, 1969
BOSE INSTITUTE
Calcutta-9

J. N. Bose

ACKNOWLEDGEMENT

Along with the students and numerous admirers of late Professor Meghnad Saha I have been feeling the need for the publication of this volume for a long time. The preliminary work for compilation was started in 1965 but the publication of the volume would not have been possible without the generous help which I have received from the Council of Scientific & Industrial Research, the Saha Institute of Nuclear Physics and the authorities of all the journals who have permitted reprinting the papers. I am indebted to Dr. Atmaram, Director General, C.S.I.R. for providing funds to undertake the publication. I thank Professor B. D. Nag and Professor D. N. Kundu of Saha Institute of Nuclear Physics for providing all facilities for the preparation of the manuscripts during the period of the publication of the volume.

I thank all the co-authors of the papers for their kind help rendered whenever wanted. For granting permission to reprint the papers free of charge I acknowledge gratefulness to the following:

The Academy of Sciences, U.P., for the papers published in Bulletin (*Bull. Acad. Sci., U.P.*);
The Asiatic Society of Bengal for the papers in their journal (*Jour. Asia. Soc. Bengal*);
The Astronomical Society of India for the papers in their journal (*Jour. Astr. Soc. Ind.*);
The Astro-Physical Journal (*Astro Phys. Jour.*);
The Calcutta University for the papers in their Journal of the Department of Science (*Jour. Dep. Sci. Cal. Univ.*);
The Harvard College Observatory for reprinting their Bulletin No. 905;
The Indian Association for the Cultivation of Science for the papers published in the Indian Journal of Physics (*Ind. Jour. Phys.*);
The Indian Chemical Society for the papers in their journal (*Jour. Ind. Chem. Soc.*);
The Indian Science News Association for the papers in the Science & Culture (*Sci. & Cult.*);
The Institute of Physics and the Physical Society of London for the paper published in the Proceedings of the Physical Society of London (*Proc. Phys. Soc. Lond.*);
The Johnson Reprint Corporation of New York for papers published in the *Physikalische Zeitschrift* (*Physik. Zeit.*);
The National Academy of Sciences, India, for the paper in their proceedings (*Proc. Nat. Acad. Sci. Ind.*);
The Secretary, National Institute of Sciences of India for the papers published originally in their Proceedings (*Proc. Nat. Inst. Sci. Ind.*) and Transactions (*Trans. Nat. Inst. Sci. Ind.*);
The Nature, London;
The Physical Review (*Phys. Rev.*), New York;
The Royal Astronomical Society of London for the paper in their monthly notices (*Mon. Not. Roy. Astro. Soc.*);
The Royal Society of London for papers in their proceedings (*Proc. Roy. Soc. Lond.*);

The Springer-Verlog, West Berlin for the papers in *Zeitschrift für Physik* (*Zeit. für Physik.*);
The Taylor Francis Ltd., London for the papers published in *Philosophical Magazine* (*Phil. Mag.*).

The papers are presented in the chronological order of their publication. There is, however, one exception. Paper No. 88 should have appeared after paper No. 14, but the copy of the paper was obtained at the last stage of the printing through the courtesy of Dr. R. V. Karandikar, Director of the Centre of Advanced Study in Astronomy, Osmania University, Hyderabad. The papers are, as far as practicable, faithful reproductions of the original. Only typographical errors have been corrected. The original diagrams have been reproduced wherever possible. But in many cases the original diagrams had to be redrawn. It has not been possible to include in this volume the many review articles and the addresses delivered by Professor Saha in different symposia and meetings. Efforts will be made to publish them in separate volumes.

I take this opportunity to thank my friends and colleagues, particularly Prof. S. B. Karmahapatro and Prof. A. M. Ghose for their assistance in the editorial work. I also thank Mr. S. C. Mukherjee and Mr. A. C. Chatterjee for their untiring help in the compilation work.

October 6, 1969

SAHA INSTITUTE OF NUCLEAR PHYSICS
Calcutta-9

SANTIMAY CHATTERJEE

CONTENTS

(Title of the paper, co-authors and reference)	Page No.
On Maxwell's Stresses: <i>Phil. Mag.</i> , Sr. VI, 33 , 256, 1917..	1
On the Limit of Interference in the Fabry-Perot Interferometer: <i>Phys. Rev.</i> , 10 , 782, 1917 ..	3
On a New Theorem in Elasticity: <i>Jour. Asia. Soc. Bengal, New Sr.</i> 14 , 421, 1918 ..	5
On the Pressure of Light (with S. Chakraborty): <i>Jour. Asia. Soc. Bengal, New Sr.</i> 14 , 425, 1918 ..	6
On the Dynamics of the Electron: <i>Phil. Mag.</i> , Sr. VI, 36 , 76, 1918 ..	9
On the Influence of the Finite Volume of Molecules on the Equation of State (with S. N. Bose): <i>Phil. Mag.</i> , Sr. VI, 36 , 199, 1918 ..	14
On the Mechanical and Electro-dynamical Properties of the Electron: <i>Phys. Rev.</i> , 13 , 34, 1919; <i>Phys. Rev.</i> , 13 , 238, 1919 ..	15
On Radiation Pressure and the Quantum Theory, A Preliminary Note: <i>Astro Phys. Jour.</i> , 50 , 220, 1919 ..	21
On the Fundamental Law of Electrical Action: <i>Phil. Mag.</i> , Sr. VI, 37 , 347, 1919 ..	23
On Selective Radiation Pressure and the Radiative Equilibrium of the Solar Atmosphere: <i>Jour. Dept. Science, Calcutta University</i> , 2 , (Physics), 51, 1920 ..	33
Note on the Secondary Spectrum of Hydrogen: <i>Phil. Mag.</i> , Sr. VI, 40 , 159, 1920 ..	37
Ionisation in the Solar Chromosphere: <i>Phil. Mag.</i> , Sr. VI, 40 , 472, 1920 ..	38
Elements in the Sun: <i>Phil. Mag.</i> , Sr. VI, 40 , 809, 1920 ..	45
On the Problem of Nova Aquila III: <i>Jour. Astr. Soc. Ind.</i> , 10 , 36, 1920 ..	51
On the Problems of Temperature Radiation of Gases (Paper C): <i>Phil. Mag.</i> , Sr. VI, 41 , 267, 1921 ..	53
The Atomic Radius and the Ionization Potential: <i>Nature</i> , 107 , 682, 1921 ..	58
On a Physical Theory of Stellar Spectra: <i>Proc. Roy. Soc. Lond.</i> , A99 , 135, 1921 ..	59
Versuch einer Theorie der physikalischen Erscheinungen bei hohen Temperaturen mit Anwendungen auf die Astrophysik: <i>Zeit. f. Phys.</i> , 6 , 40, 1921 ..	69
The Stationary H and K-lines of Calcium in Stellar Atmospheres: <i>Nature</i> , 107 , 488, 1921 ..	77
On the Ionization of Gases by Heat (with P. Gunther): <i>Jour. Dept. Sci., Cal. Univ.</i> , 4 , 97, 1922 ..	78
On the Temperature Ionization of Elements of the Higher Groups in the Periodic Classification: <i>Phil. Mag.</i> , Sr. VI, 44 , 1128, 1922 ..	82
On the Physical Properties of Elements at High Temperatures: <i>Phil. Mag.</i> , Sr. VI, 46 , 534, 1923 ..	87
On Continuous Radiation from the Sun: <i>Nature</i> , 112 , 282, 1923 ..	91
On an Experimental Test of Thermal Ionization of Elements (with N. K. Sur): <i>Jour. Ind. Chem.</i> <i>Soc.</i> , 1 , 9, 1924 ..	92
On an Active Modification of Nitrogen (with N. K. Sur): <i>Phil. Mag.</i> , Sr. VI, 48 , 421, 1924 ..	95
The Pressure in the Reversing Layer of Stars and Origin of Continuous Radiation from the Sun: <i>Nature</i> , 114 , 155, 1924 ..	98
Ionization in Stellar Atmospheres and Steric Factor: <i>Mon. Not. Roy. Astro. Soc.</i> , 85 , 977, 1925 ..	100
Influence of Radiation on Ionisation Equilibrium (with R. K. Sur): <i>Nature</i> , 115 , 377, 1925 ..	101
The Phase Rule and its Application to Problems of Luminescence and Ionization of Gases: <i>Jour. Ind. Chem. Soc.</i> , 2 , 49, 1925 ..	102
The Spectrum of Si ⁺ (once Ionized Silicon): <i>Nature</i> , 116 , 644, 1925 ..	106
On the Absolute Value of Entropy (with R. K. Sur): <i>Phil. Mag.</i> , Sr. VII, 1 , 279, 1926 ..	106
On Entropy of Radiation II (with R. K. Sur): <i>Phil. Mag.</i> , Sr. VII, 1 , 890, 1926 ..	110

	<i>Page No.</i>
On the Influence of Radiation on Ionization Equilibrium (with R. K. Sur): <i>Phil. Mag., Sr. VII</i> , 1 , 1025, 1926	112
Nitrogen in the Sun: <i>Nature</i> , 117 , 268, 1926	116
Über einen experimentellen Nachweis der thermischen Ionisierung der Elemente (with N. K. Sur & K. Majumder): <i>Zeit. f. Phys.</i> , 40 , 648, 1927	117
Über das Mainsmith-Stonersche Schema des Aufbaus der Atome (with B. B. Ray): <i>Physik Zeitschr.</i> , 28 , 221, 1927	118
Über ein neues Schema für den Atomaufbau: <i>Physik Zeitschr.</i> , 28 , 469, 1927	121
On the detailed Explanation of Spectra of the Metals of the Second Group: <i>Phil. Mag., Sr. VII</i> , 3 , 1265, 1927	125
On the Explanation of Spectra of Metals of Group II, Part II (with P. K. Kichlu): <i>Phil. Mag.</i> , <i>Sr. VII</i> , 4 , 193, 1927	130
A Note on the Spectrum of Neon: <i>Phil. Mag., Sr. VII</i> , 4 , 223, 1927	136
On the Explanation of Complicated Spectra of Elements: <i>Estratto dagli Atti del congresso Inter- nazionale dei Fisici Como-Settembre 1927 (V)</i>	140
Extension of the Irregular Doublet Law to Complex Spectra (with P. K. Kichlu): (a) <i>Ind. Jour. Phys.</i> , 2 , 319, 1928; (b) <i>Nature</i> , 121 , 244, 1928	158
The Origin of the Nebulium Spectrum: <i>Nature</i> , 121 , 418, 1928	173
The Origin of the Spectrum of the Solar Corona: <i>Nature</i> , 121 , 671, 1928	175
Negatively Modified Scattering (with D. S. Kothari and G. R. Toshniwal): <i>Nature</i> , 122 , 398, 1928	177
On the Method of Horizontal Comparison in the Location of Spectra of Elements (with K. Majumder): <i>Ind. Jour. Phys.</i> , 3 , 67, 1929	178
On New Methods in Statistical Mechanics (with R. C. Majumder): <i>Phil. Mag., Sr. VII</i> , 9 , 584, 1930	182
Colours of Inorganic Salt: <i>Nature</i> , 125 , 163, 1930	184
Über die Verteilung der Intensität unter die Feinstrukturkomponenten der Serienlinien der Wasserstoffs und des ionisierten Heliums nach der Diracschen Elektronentheorie (with A. C. Banerji): <i>Zeits. f. Phys.</i> , 68 , 704, 1931	185
The spin of the photon (with Y. Bhargava): <i>Nature</i> , 128 , 817, 1931	192
On the Colours of Inorganic Salts (with S. C. Deb): <i>Bull. Acad. Sci. U.P.</i> , 1 , 1, 1931	193
On the Absorption Spectra of Saturated Halides of Multivalent Elements (with A. K. Dutta): <i>Bull. Acad. Sci., U.P.</i> , 1 , 19, 1931	196
On the Interpretation of X-ray Term Values (with R. S. Sharma): <i>Bull. Acad. Sci., U.P.</i> , 1 , 119, 1931	199
Complex X-ray Characteristic Spectra (with S. Bhargava and J. B. Mukherjee): <i>Nature</i> , 129 , 435, 1932	205
On the Beta-ray Activity of Radioactive Bodies (with D. S. Kothari): <i>Bull. Acad. Sci., Allahabad</i> , 5 , 257, 1934	206
A Suggested Explanation of Beta-ray Activity (with D. S. Kothari): (a) <i>Nature</i> , 132 , 747, 1933; (b) <i>Nature</i> , 133 , 99, 1934	212
Inner Conversion in X-ray Spectra (with J. B. Mukherjee): <i>Nature</i> , 133 , 377, 1934	214
The Upper Atmosphere: <i>Proc. Nat. Inst. Sci. Ind.</i> , 1 , 217, 1935	215
Spectra of Comets: <i>Sci. & Cult.</i> , 1 , 476, 1936	228
Can Electrons Enter the Nucleus: <i>Sci. & Cult.</i> , 2 , 273, 1936	229
The Origin of Mass in Neutrons and Protons: <i>Ind. Jour. Phys.</i> , 10 , 141, 1936	230
A Critical Review of the Present Theories of the Active Modification of Nitrogen (with L. S. Mathur): <i>Proc. Nat. Acad. Sci. Ind.</i> , 6 , 120, 1936	235
A New Model Demountable Vacuum Furnace (with A. N. Tandon): <i>Proc. Nat. Acad. Sci. Ind.</i> , 6 , 212, 1936	238
A Century's Solar Observations: <i>Harvard College Observatory Bulletin</i> , 905, 1937	240

	<i>Page No.</i>
Experimental Determination of the Electron Affinity of Chlorine (with A. N. Tandon): <i>Proc. Nat. Inst. Sci. Ind.</i> , 3 , 287, 1937	243
Molecules in Interstellar Space: <i>Nature</i> , 139 , 840, 1937	248
On Propagation of Electromagnetic Waves through the Atmosphere (with R. N. Rai): <i>Proc. Nat. Inst. Sci. Ind.</i> , 3 , 359, 1937	249
On the Action of Ultraviolet Sunlight upon the Upper Atmosphere: <i>Proc. Roy. Soc. Lond.</i> , A160 , 155, 1937	254
On the Propagation of Electromagnetic Waves through the Earth's Atmosphere (Paper I) (with R. N. Rai & K. B. Mathur): <i>Proc. Nat. Inst. Sci. Ind.</i> , 4 , 53, 1938	263
On the Ionization of the Upper Atmosphere (with R. N. Rai): <i>Proc. Nat. Inst. Sci. Ind.</i> , 4 , 319, 1938	269
The Propagation and the Total Reflection of Electromagnetic Waves in the Ionosphere (with K. B. Mathur): <i>Ind. Jour. Phys.</i> , 13 , 251, 1939	278
On the Structure of Atomic Nuclei (with S. C. Sirkar & K. C. Mukherjee): <i>Proc. Nat. Inst. Sci. Ind.</i> , 6 , 45, 1940.. .. .	283
On a Physical Theory of the Solar Corona: <i>Proc. Nat. Inst. Sci. Ind.</i> , 8 , 99, 1942	293
Capture of Electrons by Positive Ions while passing through Gases (with D. Basu): <i>Ind. Jour. Phys.</i> , 19 , 121, 1945	307
Wave Treatment of Propagation of Electromagnetic Waves in the Ionosphere (with B. K. Banerjea): <i>Ind. Jour. Phys.</i> , 19 , 159, 1945	315
A Physical Theory of the Solar Corona: <i>Proc. Phys. Soc. Lond.</i> , 57 , 271, 1945	319
On Nuclear Energetics and Beta Activity (with A. K. Saha): <i>Trans. Nat. Inst. Sci. Ind.</i> , 2 , 193, 1946	329
On Nuclear Energetics and Beta Activity (with A. K. Saha): <i>Nature</i> , 158 , 6, 1946	349
Conditions of Escape of Radio-frequency energy from the Sun and the Stars: <i>Nature</i> , 158 , 549, 1946	354
Origin of Radio-waves from the Sun and the Stars: <i>Nature</i> , 158 , 717, 1946	355
Measurement of Geological Time in India: The Age of Rocks and Minerals (with B. D. Nagchaudhuri): <i>Trans. Nat. Inst. Sci. Ind.</i> , 2 , 273, 1947	358
On the Propagation of Electromagnetic waves through the Upper Atmosphere (with B. K. Banerjea and U. C. Guha): <i>Ind. Jour. Phys.</i> , 21 , 181, 1947	368
On the conditions of Escape of Microwaves of Radio-frequency Range from the Sun (with B. K. Banerjea and U. C. Guha): <i>Ind. Jour. Phys.</i> , 21 , 199, 1947	377
Notes on Dirac's Theory of Magnetic Poles: <i>Phys. Rev.</i> , 95 , 1968, 1949	388
Vertical Propagation of Electromagnetic Waves in the Ionosphere (with B. K. Banerjea and U. C. Guha): <i>Proc. Nat. Inst. Sci. Ind.</i> , 17 , 205, 1951	389
Occurrence of Stripped Nuclei of Neon in Primary Cosmic Rays: <i>Nature</i> , 167 , 476, 1951	401
Determination of the Electron Concentration and the Collision Frequency in the Ionosphere Layers of the O and X Waves: <i>Proc. Mixed Commission on the Ionosphere, Brussels</i> , 211, 1954	403
On Electron Chemistry and its Application to Problems of Radiation and Astrophysics: <i>Jour. Astro. Soc. Ind.</i> , 10 , 72, 1921	406

1. ON MAXWELL'S STRESSES*

(*Phil. Mag., Sr. VI, 33, 256, 1917*)

1. Maxwell¹ has shown that the mechanical action between two electrical systems at rest can be accounted for by assuming the existence of certain stresses distributed over a surface completely enclosing one of the systems. If ψ be the potential at any point due to the whole system, the X -component of the mechanical force on one of the systems can be shown to be

$$F_x = \frac{1}{4\pi} \iiint \frac{\partial \psi}{\partial x} \nabla^2 \psi \, dx \, dy \, dz, \quad (1)$$

where the integration extends over the space occupied by the first system.

2. If the force is really due to the presence of stresses on a surface enclosing the first system, we have

$$F_x = \iint X_v dS = \iint (lX_x + mX_y + nX_z) dS, \quad (2)$$

where $X_x, X_y, X_z, \&c \dots$ are the various surface-tractions, and (l, m, n) are the direction cosines of the normal to the surface.

By transforming expression (2), we obtain

$$F_x = \iiint \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right) dx \, dy \, dz.$$

$$\text{Since } \frac{1}{4\pi} \frac{\partial \psi}{\partial x} \nabla^2 \psi = \frac{\partial}{\partial x} \left[\frac{1}{8\pi} \left\{ \left(\frac{\partial \psi}{\partial x} \right)^2 - \left(\frac{\partial \psi}{\partial y} \right)^2 - \left(\frac{\partial \psi}{\partial z} \right)^2 \right\} \right]$$

$$+ \frac{\partial}{\partial y} \left[\frac{1}{4\pi} \frac{\partial \psi}{\partial x} \cdot \frac{\partial \psi}{\partial y} \right] + \frac{\partial}{\partial z} \left[\frac{1}{4\pi} \frac{\partial \psi}{\partial x} \cdot \frac{\partial \psi}{\partial z} \right],$$

$$\text{we have, putting } \frac{\partial \psi}{\partial x} = X, \frac{\partial \psi}{\partial y} = Y, \frac{\partial \psi}{\partial z} = Z,$$

$$\iiint \left\{ \frac{\partial}{\partial x} \left[X_x - \frac{1}{8\pi} (X^2 - Y^2 - Z^2) \right] + \frac{\partial}{\partial y} \left[X_y - \frac{1}{4\pi} X Y \right] + \frac{\partial}{\partial z} \left[X_z - \frac{1}{4\pi} X Z \right] \right\} dx \, dy \, dz = 0 \quad (3)$$

Maxwell concludes from this that a system of stresses

$$\begin{aligned} X_x &= \frac{1}{8\pi} (X^2 - Y^2 - Z^2), & Y_y &= \frac{1}{8\pi} (Y^2 - Z^2 - X^2), \\ Z_z &= \frac{1}{8\pi} (Z^2 - X^2 - Y^2), & X_y &= \frac{1}{4\pi} X Y, \\ Y_z &= \frac{1}{4\pi} Y Z, & Z_x &= \frac{1}{4\pi} Z X, \end{aligned} \quad (4)$$

distributed over the surface S account for the mechanical action quite satisfactorily, and therefore provide a concrete physical representation of the mechanism of electrostatic action.

3. But the expressions (4) are not complete solutions of the integral equation (3). Maxwell² himself points out that they can at best be regarded as a first step towards the solution of equation (3). Many investigators, including Sir J. J. Thomson³, have pointed out that aether cannot possibly be at rest under these stresses. Lorentz⁴ goes so far as to say that the stresses are simply mathematical fictions, which can be conveniently utilized for the calculation of radiation pressure and other allied phenomena. The object of the present paper is to show that the stresses cannot account for the energy of electrification, if the medium is to be regarded as an elastic solid.

4. The energy of a charged system can be expressed as a volume integral,

$$W = \frac{1}{8\pi} \iiint \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2 + \left(\frac{\partial \psi}{\partial z} \right)^2 \right] dx \, dy \, dz \quad (5)$$

Maxwell⁵ states that the quantity W may be interpreted as the energy in the medium due to the distribution of stresses; but the statement is not proved. The only rational meaning which we can attach to this assertion is that the energy of electrification arises from the elastic displacement of aether particles. I am not aware whether any other interpretation has been or can be given to Maxwell's statement, but it has generally been taken in this sense, though Maxwell himself is rather vague on the point. We should naturally expect that energy calculated on this understanding would lead to the expression (5), but that this is not the case will be presently shown.

5. If u, v, w be the elastic displacements of a particle of the dielectric medium, the energy of deformation or the strain-energy function is

$$\begin{aligned} W' &= \int_{\text{initial state}}^{\text{final state}} \rho (X\delta u + Y\delta v + Z\delta w) \, dx \, dy \, dz \\ &+ \int_{\text{initial state}}^{\text{final state}} (X_v\delta u + Y_v\delta v + Z_v\delta w) \, dS, \end{aligned} \quad (6')$$

¹ Loc. cit. p. 165 et seq.

² Loc. cit. p. 165. footnote

³ 'Theory of Electrons', p. 31.

⁴ 'Electricity and Magnetism', p. 165.

* Communicated by Prof. D. N. Mallik.

[†] Maxwell, 'Electricity and Magnetism', Vol. 1, Chap. V.

and this can be shown to be equivalent to

$$\frac{1}{2} \iiint (X_x e_{xx} + Y_y e_{yy} + Z_z e_{zz} + X_y e_{xy} + Y_x e_{yx} + Z_x e_{xz} + X_z e_{zx} + Y_z e_{zy} + Z_y e_{yz}) dx dy dz.$$

Assuming the aether to be isotropic and to behave as an elastic solid, we can put

$$\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \end{bmatrix} = \frac{1}{E} \begin{bmatrix} 1 & -\sigma & -\sigma \\ -\sigma & 1 & -\sigma \\ -\sigma & -\sigma & 1 \end{bmatrix} \begin{bmatrix} X_x \\ Y_y \\ Z_z \end{bmatrix},$$

$$\text{and } e_{xy} = \frac{X_y}{\mu}, e_{yz} = \frac{Y_z}{\mu}, e_{zx} = \frac{Z_x}{\mu}.$$

Then, after some calculation, the strain-energy function comes out to be

$$W' = \frac{1}{2} \frac{3(1+2\sigma)}{\epsilon(1+\sigma)} \iiint \left(\frac{R^2}{8\pi^2} \right)^2 dx dy dz \quad (6)$$

It will thus be seen that if the stresses are really existent, and if they are amenable to the ordinary laws of elasticity, the strain-energy function, or the energy of elastic deformation of the medium, is

$$\frac{3}{2} \frac{(1+2\sigma)}{\epsilon(1+\sigma)} \left(\frac{R^2}{8\pi^2} \right)^2$$

per unit volume. But this is very different from the theorem that the energy density per unit volume is $(R^2/8\pi)$ which is derived from electrostatic principles.

6. Since nothing definite is known about the elastic constants of aether, we cannot draw any conclusion from (6) about the energy distribution in aether. Maxwell's stresses are thus seen to fail to account for the energy of electrification, on the understanding that the medium behaves like an elastic solid.

7. It is well known that the energy-distribution theorem is proved on the basis of the empirical laws of electrostatics. No use is made of the stresses. The result is purely analytical, and says that if energy is distributed all over space as a continuous function with volume density $(R^2/8\pi)$, the total energy will come out to be the same as the total energy of electrification. The distinction between Maxwell's view of energy distribution as due to stresses (in the sense we have interpreted it) and the actual case can be better brought out if we adopt the following modified method of proving the energy-distribution theorem. Suppose we have an electrical system consisting of charged surfaces, and particles in a given configuration. The energy of electrification will be the same in whichever way we may bring about the final configuration. Suppose that, to start with, the charges and the charged surfaces were all at an infinite distance, and the given configuration is brought about by properly moving the charged surfaces and other discreet electrified particles. Then the energy of electrification is

$$\begin{aligned} W &= \Sigma \int e dV, \\ &= \Sigma \iint \sigma \left(\frac{\partial V}{\partial x} \delta x + \frac{\partial V}{\partial y} \delta y + \frac{\partial V}{\partial z} \delta z \right) dS, \\ &+ \Sigma \iiint \rho \left(\frac{\partial V}{\partial x} \delta x + \frac{\partial V}{\partial y} \delta y + \frac{\partial V}{\partial z} \delta z \right) dx dy dz, \end{aligned}$$

where σ is the surface density of electricity on a charged

surface, and ρ is the volume density. Since $\frac{\partial V}{\partial x}$ is the x -component of electrical force on a surface, $\sigma \frac{\partial V}{\partial x}$ is the x -component of mechanical action per unit surface. Similarly, $\rho \frac{\partial V}{\partial x}$ is the x -component of mechanical force per unit volume of electrified particles. We can therefore put

$$W = \Sigma \iint (X_v \delta x + Y_v \delta y + Z_v \delta z) + \Sigma \iiint (X \delta x + Y \delta y + Z \delta z).$$

8. Comparing this expression for energy with the expression (6)

$$W' = \iint (X_v \delta u + Y_v \delta v + Z_v \delta w) + \iiint \rho (X \delta u + Y \delta v + Z \delta w), \quad (6'')$$

we see that in the present case (X_v, Y_v, Z_v) are the components of surface-tractions on a charged surface, and (X, Y, Z) are the body-forces on electrified particles. The existence of these forces can be experimentally demonstrated, and they exist only in regions occupied by electricity; elsewhere they are nil. The energy of electrification is derived from the work done in the actual displacements $(\delta x, \delta y, \delta z)$ of these charged regions towards each other. On the other hand, (X_v, Y_v, Z_v) in $(6'')$ are the tractions on a surface enclosing some of the charged regions, and $\delta u, \delta v, \delta w$ are their elastic displacements. We may by special assumption identify the two systems of surface-tractions and body-forces, but the actual displacements $(\delta x, \delta y, \delta z)$ and the elastic displacements $(\delta u, \delta v, \delta w)$ cannot be identified in any way. The two expressions represent fundamentally different quantities.

9. The fact that radiant energy would exert a definite amount of pressure on material surfaces was first predicted by Maxwell on the hypothesis of dielectric stresses. Now that radiation pressure is an experimental fact, it has been supposed by some physicists that Maxwell's stresses must have a material existence. But it is well known that radiant energy can be deduced independently of the stresses. Bartoli has shown that the pressure of radiant energy can be deduced from thermodynamic principles. Planck⁶ has deduced it from electrodynamical principles, assuming that the perfect reflector is a super-conductor of electricity. This is an ideal limiting case of the experimental fact that good conductors of electricity are also good reflectors of radiant energy. The electric vector accompanying a ray of light gives rise to a finite charge on the surface of the super-conductor and a finite current within the conductor. The charge exerts a negative pressure on the surface, while the current, in presence of the field of the magnetic vector accompanying the ray, produces a mechanical force in the contrary direction. The resultant of the two, when averaged statistically, yields the radiation pressure. How far these theories are consistent with the theory of stresses may form a subject for interesting investigations.

My best thanks are due to Prof. D. N. Mallik for his kind help and encouragement.

⁶ Planck, *Wärmestrahlung*, 2nd Edn., pp. 49 et. seq.

2. ON THE LIMIT OF INTERFERENCE IN THE FABRY-PEROT INTERFEROMETER

(*Phys. Rev.*, **10**, 782, 1917)

When a monochromatic source of radiation (for example, that given by a vacuum tube, when excited by an electrical discharge) is examined by a Fabry-Perot interferometer, we obtain bright and narrow rings of maximum intensity separated by wide dark intervals. If the distance between the plates of the etalon be gradually increased, the maxima gradually decrease in brightness, until we reach a limit where we can no longer distinguish between the maxima and the minima. The theory of this phenomenon has been worked out by Lippich, Lord Rayleigh¹, and Schönrock², and is shown to be due to the fact that the emission centres (in this case the gaseous atoms) being in motion, a sort of Doppler-Fizeau effect is produced in the line of vision of the observer. They have shown that when the pressure is small, the critical distance D (or the limit of interference) is connected by the following formula with the wave-length (λ) of light, the temperature (T) of the tube, and the mass (M) of the emission centres:

$$\frac{D}{\lambda} = A \sqrt{\frac{M}{T}} \quad (a)$$

This theorem has been made the basis of a wide series of experiments by Michelson³, and the French School of opticians including Fabry, Perot and Buisson⁴. Among the various problems to which the formula (a) has been applied may be mentioned the following:

(i) The temperature of the discharge tube when emitting a monochromatic light.

(ii) The temperature of stars and nebulae.

(iii) Mass of the emission centres of lines in the spectrum.

Probably the mass of the emission centres of many lines of unknown origin in the solar corona and many nebulae (e.g., $\lambda = 5007\text{\AA.U.}$) which are attributed to hypothetical elements⁵, coronium and nebulium may be determined by this method.

The value of the constant A is of much use in all these investigations, and it is generally deduced from theoretical considerations. While going through the literature on the subject, I found that A is generally calculated from approximate and not altogether satisfactory considerations, though an exact solution is not difficult. My object in the present communication is to effect this improvement in the

theory. For this we must begin with a preliminary scrutiny of the theory of the Fabry-Perot interferometer.

The Fabry-Perot interferometer consists of two plane parallel plates of glass, both heavily silvered on the inside. If a ray of light is sent through the plates, it undergoes several internal reflections, and at each reflection from either surface, a part issues out. Every incident ray is thus subdivided into a large number of parallel rays. If the angle of incidence is very small, almost normal, as is the case in practice, the number would be infinite. Let us confine our attention to the rays issuing on the side further from the source of light. The parallel rays issuing at some particular angle have path differences amounting to $2d \cos \alpha$, $4d \cos \alpha$, $6d \cos \alpha$, etc., according as they have suffered double reflection once, twice, thrice or any number of times. When these rays are brought together by a converging lens we shall have the interference phenomena. The parallel system is composed of rays transmitted directly, *i.e.*, without reflection—this ray can be represented by $E_0 \cos nt$; rays suffering reflection twice, four times, etc. Since at each double reflection there is a retardation in phase amounting to $2\pi \Delta/\lambda$ and the intensity is reduced by a fraction f , we can represent the rays by the equations

$f E_0 \cos (nt - \delta)$, $f^2 E_0 \cos (nt - 2\delta)$, $f^3 E_0 \cos (nt - 3\delta)$ where we put

$$\Delta = 2d \cos \alpha \text{ and } \delta = \frac{2\pi \Delta}{\lambda}.$$

The resultant ray is now represented by

$$\begin{aligned} E &= E_0 \{ \cos nt + f \cos (nt - \delta) + f^2 \cos (nt - 2\delta) + \dots \} \\ &= E_0 [\cos nt \{ 1 + f \cos \delta + f^2 \cos 2\delta + \dots \} + \sin nt \{ f \sin \delta + f^2 \sin 2\delta + \dots \}] \\ &= E_0 \left[\cos nt. \frac{1 - f \cos \delta}{1 - 2f \cos \delta + f^2} + \sin nt. \frac{f \sin \delta}{1 - 2f \cos \delta + f^2} \right]. \end{aligned}$$

Therefore the intensity

$$I = I_0 \frac{1}{1 - 2f \cos \delta + f^2} = \frac{I_0}{(1-f)^2} \cdot \frac{1}{1 + \frac{4f}{(1-f)^2} \sin^2 \frac{\delta}{2}}.$$

This is the ordinary theory of the interferometer. The intensities of the maxima and the minima are all in the

ratio of 1 : $\frac{1}{1 + \frac{4f}{(1-f)^2}}$.

¹ Lord Rayleigh, *Phil. Mag.*, November 1915.

² Schönrock, *Ann. D. Physik.*, 1907, Bd. 22, 1907.

³ Michelson, *Astrophysical Journal*, 1895, Vol. (ii), p. 251.

⁴ Buisson et Fabry, *Journal de Physique*, tome 11, 1912, p. 442-464.

⁵ Nicholson, *Phil. Mag.*, 1911, Vol. 22, p. 864.

If we take $f=.75$, this ratio becomes 49 : 1, the angular separation being $\alpha=\lambda/\Delta$. If the theory held rigorously, we could observe interference with large values of Δ . But this is not the case. For example, in the case of the sodium D_1 line, no interference can be obtained when Δ exceeds 3 cm. This is due to the fact that the radiant particles are themselves in motion, and the theory cannot be perfect unless we take account of this fact.

According to Maxwell's distribution law, the number of particles having their velocity between v and $v+dv$ is $Ae^{-\beta v^2} dv$. The frequency of radiation emitted by these particles is $n [1+(v/c)]$ where n is the wave frequency of light emitted by particles at rest. In the expression for retardation in phase, we must therefore replace λ by $\lambda/[1+(v/c)]$ and write $\frac{2\pi\Delta}{\lambda} [1+(v/c)]$ in place of $2\pi\Delta/\lambda$.

The intensity of light emitted by molecules having their velocity between $v+dv$ and v is

$$dI=B \frac{e^{-\beta v^2} dv}{1-2f \cos \delta [1+(v/c)] + f^2}.$$

The total intensity

$$I=B \int_{-\infty}^{\infty} \frac{e^{-\beta v^2} dv}{1-2f \cos \delta [1+(v/c)] + f^2}.$$

We have by trigonometry,

$$\frac{1-f^2}{1-2f \cos \delta + f^2} = 1 + 2f \cos \delta + 2f^2 \cos 2\delta + \dots$$

Now, we have

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-\beta v^2} dv \cdot \sin \frac{n\delta v}{c} &= 0, \\ \int_{-\infty}^{\infty} e^{-\beta v^2} dv \cdot \cos \frac{n\delta v}{c} &= \sqrt{\frac{\pi}{\beta}} e^{-\left(\frac{1}{4\beta}\right) (n\delta/c)^2}. \end{aligned}$$

We have therefore

$$I = \frac{B_0}{1-f^2} \sqrt{\frac{\pi}{\beta}} \left[1 + 2 \sum_1^{\infty} f^n e^{-\left(\frac{1}{4\beta}\right) (n\delta/c)^2} \cos n\delta \right].$$

Now let I_1 =the maximum value of I , corresponding to $n\delta=0$,

I_2 =the minimum value of I , corresponding to $n\delta=\pi$.

Then the visibility factor V is, according to Michelson

$$\frac{I_1-I_2}{I_1+I_2} = \frac{f e^{-\left(\frac{1}{\beta}\right) \left(\frac{\pi\Delta}{\lambda c}\right)^2} + f^3 e^{-\left(\frac{9}{\beta}\right) \left(\frac{\pi\Delta}{\lambda c}\right)^2} + \dots}{\frac{1}{2} + f^2 e^{-\left(\frac{2}{\beta}\right) \left(\frac{\pi\Delta}{\lambda c}\right)^2} + f^4 e^{-\left(\frac{4}{\beta}\right) \left(\frac{\pi\Delta}{\lambda c}\right)^2} + \dots}.$$

Now $(1/\beta) \left(\frac{\pi\Delta}{\lambda c}\right)^2$ is of the order 10^8 . We can, therefore, safely omit terms containing f^2, f^3 , etc.

$$V \text{ is therefore } = 2f e^{-\left(\frac{1}{\beta}\right) \left(\frac{\pi\Delta}{\lambda c}\right)^2}.$$

From the kinetic theory of gases, we have $\beta=(m/2KT)$
 $=(wM/2KT)$,

where m =weight of the radiant atom in grams,
 w =weight of the hydrogen atom,
 M =atomic weight of the radiant gas,
 K =universal gas constant,
 T =temperature.

Then we have, since

$$-\frac{1}{\beta} \left(\frac{\pi\Delta}{\lambda c}\right)^2 = \log_e \left(\frac{V}{2f}\right), \frac{\Delta}{\lambda} = \frac{c}{\pi} \sqrt{\frac{wM}{2KT} \log_e \left(\frac{2f}{V}\right)}. \dots\dots(b)$$

Lord Rayleigh took account of the first two interfering beams only, but by this he had evidently the Michelson interferometer in his mind. But I think that when we are applying the result to the Fabry-Perot interferometer, we should take into account all the infinite number of interfering beams, and the effect of reflection. This is exactly what has been done in the present communication.

The exact evaluation of the constant $\frac{c}{\pi} \sqrt{\frac{w}{2K} \log_e \left(\frac{2f}{V}\right)}$,

cannot be done unless the reflecting power of the plates, and the value of V be known. f will depend upon the silvering of the plates, while V will vary with the observer. Thus Lord Rayleigh takes the visibility factor equivalent to .025, while Schönrock takes it equivalent to .05. Assuming that $V=.025$ and $f=.75$, we have

$$\frac{\Delta}{\lambda} = 1.50 \times 10^6 \sqrt{\frac{M}{T}},$$

while according to Lord Rayleigh

$$\frac{\Delta}{\lambda} = 1.42 \times 10^6 \sqrt{\frac{M}{T}}.$$

As it is, the discrepancy between the two values if calculated by two different methods is not much. But for particular apparatus, and for particular observers, the discrepancy may be considerable. It is to be hoped that investigators will take notice of these facts.

Calcutta University College of Science,
 July 7, 1917.

3. ON A NEW THEOREM IN ELASTICITY

(*Jour. Asia. Soc. Bengal, New Ser., 14, 421, 1918*)

1. The Equations of motion of an elastic system are¹

$$\left. \begin{aligned} \rho \ddot{u} &= \rho X + \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \\ \rho \ddot{v} &= \rho Y + \frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} \\ \rho \ddot{w} &= \rho Z + \frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} \end{aligned} \right\} \quad (1)$$

Multiplying the equations by u, v and w , and adding, we have,

$$\begin{aligned} \therefore u \ddot{u} &= \frac{1}{2} \frac{d^2}{dt^2} (u^2) - \dot{u}^2, \\ \frac{\rho}{2} \frac{d^2}{dt^2} (u^2 + v^2 + w^2) &- \rho (\dot{u}^2 + \dot{v}^2 + \dot{w}^2) \\ &= \rho (Xu + Yv + Zw) + u \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right) \\ &+ v \left(\frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} \right) + w \left(\frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} \right) \quad (2) \end{aligned}$$

Now multiplying by $(dx \cdot dy \cdot dz \cdot dt)$, and integrating we have,

$$\begin{aligned} \therefore \text{since } \iiint u \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right) dx dy dz &= \iiint u X_n dS \\ &- \iiint \left(X_x \frac{du}{dx} + X_y \frac{du}{dy} + X_z \frac{du}{dz} \right) d\Omega. \\ \iiint \int_0^{\tau} \frac{\rho}{2} \frac{d^2}{dt^2} (u^2 + v^2 + w^2) dt d\Omega &- \iiint \int_0^{\tau} 2T dt d\Omega \\ &= \iiint \int_0^{\tau} \rho (Xu + Yv + Zw) dt d\Omega \\ &+ \iiint \int_0^{\tau} (X_n u + Y_n v + Z_n w) dS dt - \iiint \int_0^{\tau} 2W d\Omega dt, \end{aligned} \quad (3)$$

where

$$2W = X_x e_{xx} + Y_y e_{yy} + Z_z e_{zz} + X_y e_{xy} + X_z e_{xz} + Y_z e_{yz} \quad (3)$$

Denoting by $\bar{T}$ the time-average of kinetic energy per unit volume, and by $\bar{W}$ the time-average of the potential energy per unit volume, we have

$$\iiint (\bar{W} - \bar{T}) d\Omega = \frac{1}{2\tau} \iiint \int_0^{\tau} \rho (Xu + Yv + Zw) dt d\Omega$$

$$\begin{aligned} &+ \frac{1}{2\tau} \iiint \int_0^{\tau} \rho (X_n u + Y_n v + Z_n w) dS dt \\ &- \frac{1}{\tau} \iiint \left[\frac{\rho}{4} \frac{d}{dt^2} (u^2 + v^2 + w^2) \right]_{t=0}^{t=\tau} d\Omega \quad (4) \end{aligned}$$

2. If we now take a closed volume Ω and $\bar{W}, \bar{T}$ denote the average values over time as well as over space, we shall have

$$\begin{aligned} \bar{W} - \bar{T} &= \frac{1}{2\Omega\tau} \iiint \int_0^{\tau} \rho (Xu + Yv + Zw) d\Omega dt \\ &+ \frac{1}{2\Omega\tau} \iiint \int_0^{\tau} (X_n u + Y_n v + Z_n w) dS dt \quad (5) \end{aligned}$$

Since if τ be sufficiently large, the function $\frac{d}{dt} (u^2 + v^2 + w^2)$ will have the same value at the beginning and end of the process if the motion be vibratory, for then τ will contain a large number of periods.

3. The analogy of theorem (5) to Clausius's² Virial Theorem is quite evident. According to the virial theorem, we have

$$-T = \frac{1}{2} \sum \sum xX + yY + zZ,$$

where T = kinetic energy of the number of particles within unit volume, (X, Y, Z) = force components on the particle which occupies the point (x, y, z) .

4. A number of interesting applications are at once suggested.

Suppose the motion to be vibratory. Then if the body forces be nil, the average kinetic energy will be equivalent to the average potential energy if

- (i) the surface tractions be nil, or constant, as in the case of the vibration of a supported rod, or plate with free ends,
- (ii) the surface displacement be zero,
- (iii) if part of the surface be under zero or constant stress and part under varying stress with no surface displacement (e.g. the case of a clamped rod, or string stretched between two points).

These theorems are of course well known, and can be deduced in other ways.

¹ Love's Elasticity, p. 83.

² Vide Jeans' Dynamical Theory of Gases, Second Edition, p. 141.

4. ON THE PRESSURE OF LIGHT

M. N. SAHA AND S. CHAKRAVARTI

(*Jour. Asia. Soc. Bengal, New Ser.*, **14**, 425, 1918)

The object of the present paper is to describe a simple apparatus by means of which the pressure of light can be easily demonstrated, and qualitatively measured with the entire elimination of all sorts of disturbing effects. The materials required are not difficult to procure, and are readily available in all well-equipped laboratories.

We wish first to give a short history of the subject and a short sketch of the theory¹. As early as the seventeenth century Kepler supposed that light exerted a pressure on surfaces on which it is incident. The hypothesis was called into being for explaining the tails of comets.

With the rise of Newton's corpuscular theory of light, the pressure no longer remained a guess, but could be deduced from that theory. An elaborate series of experiments for detecting the pressure were instituted by De Mairan (1754), and later on by Du Fay (1756), but the results were entirely negative. Later on, the failure of these experiments were used as arguments against the validity of the corpuscular theory of light.

But interest in the subject was again revived when Maxwell², in the year 1873, predicted that even on the basis of the electro-magnetic theory of light, radiant energy should exert a pressure on a surface on which it is incident. But the amount of pressure is extremely small. It can be shown that if light consists of unidirectional rays, the pressure amounts to $\frac{1}{c}$ (amount of radiant energy falling on unit surface per unit of time, measured in absolute units), where c is the velocity of light, and the surface is a perfectly absorbing one, e.g. a surface coated with lamp-black.

If the surface on which the light is incident be perfectly reflecting, the pressure is just double. But if, on the other hand, the surface be transparent (e.g. glass), there will be no pressure at all, or more accurately a very small amount of pressure depending on the small amount of reflection from the glass surface.

The occurrence of the term c in the denominator makes the pressure extremely small. Let us take for example the pressure exerted by solar light. The amount of energy which is delivered by the sun on unit surface placed normally to the rays of the earth is equivalent to 2.4 calories per minute.

The pressure therefore

$$= \frac{2.4 \times 4.2 \times 10^7}{3 \times 10^{10} \times 60 \times 981} \text{ gms. weight} = .56 \times 10^{-7} \text{ gms. weight.}$$

By using the arc, or a very high candle power filament lamp (1500 wt/½ wt. for example), and by concentrating the light by means of a lens of large aperture, the pressure can be increased to about 100 times. But still it is extremely small.

It was for demonstrating the pressure of light that Crookes³ was led to invent his famous "radiometer". As is well known, this consists of a delicate cross of glass or mica vanes suspended on a pivot and enclosed within a glass cylinder from which air can be pumped off at will. The alternate faces of the vanes are covered with lamp-black. When light falls on the vanes it begins to rotate rapidly about the axis.

Crookes was inclined to explain this motion as being due to the pressure of radiant energy, but Zöllner⁴ showed that the effect observed was rather spurious, and exceeded theoretical pressure by at least 10³ times. He showed that the effect was really due to the unequal heating of the two sides of the vanes.

Zöllner tried to observe the effect by another arrangement. Two thin discs of silvered or blackened glass, or metal, were suspended at the ends of the horizontal arm of a thin cross of glass-rods and the whole was suspended by means of glass fibres within a closed vessel, from which air can be pumped out at will. A galvanometer mirror is attached to the vertical part, with its plane at right angles to the plane of the vanes. But with light incident on the vanes, the deflection observed was very irregular, and sometimes was completely in the wrong direction.

But in spite of repeated failures to detect the pressure of radiation, theoretical investigation had, in the meantime, been advanced so far that it was not possible to deny its existence.

We have seen that the pressure of light was deduced by Maxwell from the electromagnetic theory of light, by using an argument involving the assumption of pressures and tensions across and along tubes of force. But Bartoli⁵ showed in 1877 that the pressure could also be deduced by means of thermodynamic reasoning involving only the two laws of thermodynamics, and was in amount just the

¹ For the historical part, see Lebedew, *Ann-d. Phys.*, Bd. 6, p. 433; and Nichols and Hull, *Phys. Rev.*, 1903.

² Maxwell, *Electricity and Magnetism*, Vol. II, p. 792.

³ *Phil. Trans.*, 1874, Vols. 164, p. 501.

⁴ *Pogg. Ann Bd.*, 160, p. 154, 1877 (suggested by Maxwell).

⁵ Bartoli, *Nuovo Cimento*, 15, p. 195, 1883.

same as is obtained from Maxwell's theory. Bartoli's argument being based on the surer basis of thermodynamics, seemed to carry conviction in all quarters about the real existence of the pressure.

The long-expected pressure was at last observed by Lebedew, and almost simultaneously by Nichols and Hull in 1901, by different modifications of Zöllner's unsuccessful experiment.

Lebedew's method was to replace the rather thick glass vanes by means of very thin platinum foils (diameter 5 mm., thickness .02 mm.) whereby any difference of temperature on the two sides is instantly equalised. The radiometer action is directly proportional to the difference of pressure on the two sides, and the pressure of gas within the vessel. Lebedew reduced the pressure to about $1/20000$ th of a mm. and was almost able to eliminate the radiometer action, and verify the pressure qualitatively to about 20% of the theoretical pressure.

The early experiments of Nichols and Hull were undertaken in order to investigate the different disturbing effects in the apparatus of Zöllner. They found that the total disturbing effect is the resultant of the following:—

- (i) the radiometer action—due to the unequal heating of the two sides of the vane;
- (ii) convection currents—due to the rush of air towards the parts warmed by the passage of the pencil of rays;
- (iii) a rocket action—due to the escape of particles of gas from the surface of the vanes when these are heated by the incident light.

By a series of elaborate investigations extending over three years, Nichols and Hull were able to get rid of these effects. They found that the convection effect could be reduced by making the vanes exactly vertical, for then the flow of air becomes tangential to their surface. The rocket action, and the radiometer action were found to balance at a pressure of 16.5 mm., and deflections were therefore observed with this pressure in the vessel. The vanes were of thin glass with one face silvered; for further information on the point reference should be made to the original paper.

Finally, Hull⁶ evolved out an arrangement by means of which the disturbing effects could be entirely eliminated. The silvered side of a thin cover-glass was placed in contact



FIG. 1

with the blackened side of a similar glass and the whole was enclosed by means of two other thin glasses, as shown in the figure. Two such cells were mounted upon the opposite ends of the torsion arm which was suspended by means of a thin quartz fibre within a glass cylinder. When

light falls on the vanes, the two sides are of course unequally heated. But as the air on the two sides is enclosed within a glass cylinder, it forms one single system with the glass vessel—action and reaction being equal, the radiometer action is entirely eliminated.

We have found the extra glass cell to be redundant. The silvered sides of two thin cover-glasses were put one upon the other and connected to each other by means of a trace of Canada balsam on the fringes. Similarly, we prepared a lampblackened surface. We have thus in these vanes very thin films of totally reflecting and totally absorbing material enclosed within equal thicknesses of glass on either side. When light previously filtered of all rays capable of heating glass, is allowed to fall on one of the vanes, say the silvered one, the glass surface is not at all heated by the passage of the rays, which have been previously passed through sufficiently thick glass lenses. The two sides of the film are instantly raised to the same temperature (because they are extremely thin and there being equal thicknesses of glass on the two sides, they are equally heated by conduction). Thus the radiometer action is entirely eliminated.

It will be thus seen that in our arrangement we have combined the arrangements of Lebedew as well as Hull's method, without the additional encumbrance of extra glass cells.

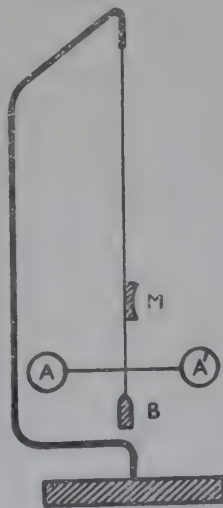


FIG. 2

DESCRIPTION OF THE APPARATUS

The vanes were suspended on the opposite arms of the torsion balance: *vide* fig. 2. (M) is a galvanometer mirror placed at right angles to the plane of the vanes, with a small piece of steel on its back. (B) is a small brass weight for steadying the balance. The whole is suspended by means of a glass fibre and enclosed within a bell-jar which is connected to a pump and a manometer.

The deflection is observed from the excursion of a spot of light reflected from (M) in the usual lamp and scale arrangement. The dimensions are

Diameter of the cover glasses	= 1.8 cm.	}
Thickness of the cover glasses	= .083 mm.	
Weight of the silvered vane	= .105 gm.	
Weight of the lampblackened vane	= .128 gm.	
Length of the arm	= 2 cm.	
Weight of B	= .5 gm.	

The pressure within the bell-jar is reduced to about 1 to 2 cms. of mercury. It is extremely important that the joints

⁶ Hull, *Phys. Rev.*, May 1905.

should be all air-tight, for the slightest leakage of air may produce disastrous effects. After pumping out we allowed the apparatus to stand for 3 days in order to be sure that it was quite air-tight. The vanes should be placed symmetrically just about the centre of the glass vessel, otherwise currents of air which are set up in the vessel by the passage of rays and turned off by the sides of the vessel may produce disturbing effects. These effects become smaller, the smaller the pressure inside the vessel.

Theory of the Apparatus:

The equation of motion of the vanes is given by—

$$I \frac{d^2\theta}{dt^2} + k \frac{d\theta}{dt} + \mu\theta = L \quad (i)$$

where I (moment of inertia of the system about the fibre, k viscosity factor, μ is the torsional coefficient, θ =angle of rotation, L moment of the force of pressure about the axis of rotation (i.e. the fibre).

$$\text{The solution is } \left(\theta - \frac{L}{\mu}\right) = Ae^{-\frac{k}{2I}t} \cos(nt + \alpha) \quad (ii)$$

$$\text{where } n^2 = \frac{\mu}{I} - \frac{k^2}{4I^2} \quad (iii).$$

After a sufficiently large time the deflection should become steady if the disturbing causes are entirely absent. Let α denote this steady deflection.

Now $L = pl$, where p =total pressure (or thrust) on the surface and l =distance of the centre of the disc from the axis of rotation. The light should be concentrated on the centre of the disc. Let α be the steady deflection. Then

$$p = \frac{\mu\alpha}{l}.$$

The constant μ is obtained from observations of the free period of oscillation of the system.

$$\text{From (ii) we see that } \frac{\mu}{I} = n^2 + \frac{k^2}{4I^2}.$$

$$\text{Now } n = \frac{2\pi}{T}, \text{ and } \frac{k^2}{4I^2} = \left(\frac{\beta}{T}\right)^2, \text{ where } \beta = \text{logarithmic}$$

decrement of the amplitude.

$$\therefore \frac{\mu}{I} = \left(\frac{2\pi}{T}\right)^2 + \left(\frac{\beta}{T}\right)^2 = \frac{1}{T^2} (4\pi^2 + \beta^2) \quad (iv)$$

Now I can be easily calculated from the weight and the dimensions of the system. μ can therefore be easily calculated from formula (iv).

In our experiment $l = 2.65$ c.m. and $\alpha = 6.27 \times 10^{-5}$ so that a deflection of (1 mm.) at a distance of 1 metre corresponded to a total pressure of

$$\frac{6.27 \times 10^{-5}}{2.65} = 2.36 \times 10^{-5} \text{ dynes.}$$

The time period was 32 seconds and the logarithmic decrement was $\beta = .310$, and $I = 1.67$ units.

MEASUREMENT OF ENERGY.

Owing to lack of means at our disposal the amount of energy falling upon the surface could not be properly measured. Lebedew allowed the light to fall on a copper calorimeter placed in the same position as the vanes, and the amount of energy absorbed was obtained by noting the rise in temperature of the calorimeter within a given period of time.

Nichols and Hull's method was more ingenious. A thin disc of silver of the same size as the vane was coated with lampblack. Two holes were bored on the sides through which a copper-constantan couple passed. The other end of the couple passed through a sensitive galvanometer. This apparatus was previously standardised by putting it in different baths. The light was allowed to fall on the disc for some time and the rise in temperature was obtained from the throw of the galvanometer.

The source of light in Lebedew and Hull's experiment was an arc which as is well known is very unsteady. In our early experiments we used the arcs but in the latest experiment the source of light was a (3000 c.p.) Tungsten filament lamp supplied by Messrs. Westinghouse & Co. The light from this source is very steady. The lamp was placed in a horizontal position (i.e. with its filament in a vertical circle) at a distance of 50 to 70 cms. from the diaphragm which contained a short focus lens of 6.5 cms. aperture. By adjusting the lens the filament was completely focussed on the vanes. An upper limit to the amount of energy falling on the vane per second can be thus obtained. By means of an ammeter we found that the lamp consumed a current 6.6 amps. under a pressure of 220 volts. The amount of energy passing through the lens and focussed on the vanes is therefore given by

$$\frac{220 \times 6.6 \times 10^7}{4\pi (d)^2} \pi (3.25)^2 \text{ ergs per sec.}$$

The whole pressure on the silvered surface is therefore

$$\frac{E}{c} (1 - \epsilon) (1 + \rho)$$

where c =velocity of light and ϵ =fraction of energy absorbed by and reflected from glass surfaces (lens and containing vessels) and ρ =fraction of energy reflected from the silvered face.

RESULTS OF OBSERVATIONS.

In our preliminary blank experiment with the arc, we found that for the period for which the arc remains steady, the deflection remains quite steady and follows very faithfully the fluctuations of the arc. When the positive pole was focussed the deflection observed was generally 3 to 4 times the deflection for the negative pole. When all the precautions above mentioned were taken, the deflection

was found to be always in the right direction. When the filament lamp was used as the source of light, all irregularities due to the variation of the source of light vanished. As soon as light is struck, the spot of light slowly creeps up towards the new position of equilibrium about which it oscillates in accordance with the equation (i).

Ultimately the oscillation dies away and the spot becomes quite steady, which could be maintained for 15 minutes (we did not try to keep the spot steady for a greater length of time because the tungsten filaments, being kept in a horizontal position, are gradually deformed on account of their plasticity at the high temperature within the lamp).

In one set of experiments one of the vanes was silvered while the other consisted of two clear pieces of microscopic cover glass. We found that when light was allowed to fall on the clear glass surface there was practically no deflection. In another set of experiments one of the vanes was silvered and the other was lampblackened. It was found that generally if the source of light was not too intense, the deflection of the black surface was approximately one half of that of the silvered one. If the source of light was very intense so much heat was absorbed that the junctions (which were all of shellac) melted off. Quantitative experiments were therefore impossible with that surface.

One of the results of our quantitative experiments is given below:—

Mean deflection (mean of several experiments)	=28.5 Divns.
Distance of the scale from the mirror	=100 cm
Distance "d" of the plane of the filament from the diaphragm	=73 cm

Therefore the upper limit of the total theoretical pressure

(without allowing for absorption or reflexion) is equal to

$$2 \times \frac{6.6 \times 220 \times 10^7 \times (3.25)^2}{4 \times 73^2 \times 3 \times 10^{10}} = 4.8 \times 10^{-4} \text{ dynes} \quad (\text{A}).$$

The pressure calculated from deflections is equal to

$$2.3 \times 10^{-5} \times 14.25 = 3.33 \times 10^{-4} \text{ dynes} \quad (\text{B}).$$

The observed pressure is about 70 per cent of the expression (A), which is the pressure calculated on the supposition that the whole amount of energy given out by the filament is freely transmitted by the various glass media, and is totally reflected by the silvered surface. As a matter of fact, none of these assumptions is correct. If T is the fraction of total energy transmitted by thick glass, and ρ be the reflecting power of a silver glass-surface the actual pressure should be

$$P_0 \frac{T}{2} (1 + \rho) (1 - \epsilon)$$

where P_0 is the quantity (A).

According to the experiments of Rubens and Hagen⁷ $\rho = 90.5\%$ unfortunately no data is available for the transmission coefficient, but on account of the preponderance of rays of short wave length in the spectrum of the light from a tungsten filament, it cannot be less than 80%.

Considering these facts, we are probably justified in asserting that the agreement between observed and theoretical values is at least qualitatively quite good. On a future occasion we hope to return to the problem of a rigorous quantitative determination of total incident energy.

In conclusion, we beg to record our best thanks to Prof. C. V. Raman, and the teaching staff of the University College of Science, for the interest they have taken in the work; and to Mr. N. Basu, B.Sc., for much useful help.

⁷Obtained by extrapolation from the data of Rubens and Hagen on the supposition that the maximum emission of energy from a tungsten filament is at 1μ [Kohlrausch, *Praktische Physik*, Tabellen].

5. ON THE DYNAMICS OF THE ELECTRON*

(*Phil. Mag.*, *Sr. VI*, **36**, 76, 1918)

Mass as a fundamental physical concept has been introduced into Physics by Newton's Second Law of Motion, which may be said to form the corner-stone of classical Mechanics. But in spite of its splendid success, physicists have always encountered some difficulty in realising mass as a fundamental physical concept in the same sense as the concepts of time and space. The fundamental object of mechanics is to provide a scaffolding by means of which the motion of material bodies can be surveyed and followed,

when these are subjected to various disturbing influences. Some hypothesis must be introduced for taking into account the influences of these disturbing agencies. The question is: "Are Newton's Second Law of Motion and the ideas underlying it quite sufficient for all possible cases of motion, or are we to search for some more general principle?" Some physicists are in fact in favour of introducing Energy as a more fundamental physical concept than Mass, thereby basing the Science of Mechanics on various Energy-theorems.

So long as we hold to the principle of invariability of

*Communicated by Prof. A. W. Porter, F.R.S.

mass, there can of course be no question about the utility of the second law. But in the electron we have a physical entity which defies this limitation. If we want to survey its motion, and have no other means of doing so than classical mechanics, we must ascribe to it a certain mass, but for aught we know this mass is neither definite nor invariant during motion. Consequently the scaffolding which enables us to study and survey the motion of material (i.e. non-electrical) particles breaks down in this case. Some other system of Mechanics other than Newtonian must be formulated. In this attempt, we must remember that the electric charge is the only invariant physical quantity, consequently in place of mass, this quantity ought to appear in the equation of motion. We must also take cognisance of the newly discovered relations between time and space which are embodied in the Principle of Relativity.

I may be allowed to remark at this place that though the inadequacy of classical mechanics for studying the motion of electrons is now admitted on all hands, and many attempts are being made for formulating the exact dynamics of the electron,—the authors of many of these theories have not been able to rid themselves of the preconceived ideas of classical mechanics. I shall, in the first place, explain my own method, point out the characteristic features of my theory, and then compare it with other theories.

1.

The equations of motion of a material particle are derived from Newton's Second Law of Motion—rate of change of momentum is proportional to the force applied. Combining this principle with the principle of constancy of mass during motion, we obtain

$$m \frac{d^2 x}{dt^2} = X, \quad m \frac{d^2 y}{dt^2} = Y, \quad m \frac{d^2 z}{dt^2} = Z.$$

The terms $m \frac{d^2 x}{dt^2}$, $m \frac{d^2 y}{dt^2}$, $m \frac{d^2 z}{dt^2}$ are known as the compo-

nents of the "Effective Force", and the law may be expressed by saying that the "Effective Force" is equivalent to the "Impressed Force".

In the case of the Electron, we hold to the axiom that the "Effective Force is equivalent to the Impressed Force". No *prima facie* reason can be given for the introduction of this hypothesis, just as in the case of the motion of material bodies. It is to be justified by its success in dealing with the problem at hand.

2.

The Impressed Force on the electron can be easily calculated with the aid of Lorentz's Theorem of Ponderomotive Force. If (X, Y, Z) be the components of the electric

field, (L, M, N) be the components of the magnetic field at any point, and ρ be the density of electricity, the components of the force per unit volume at the point are

$$\left. \begin{aligned} f_x &= \rho \left[X + \frac{1}{c} (v_2 N - v_3 M) \right] \\ f_y &= \rho \left[Y + \frac{1}{c} (v_3 L - v_1 N) \right] \\ f_z &= \rho \left[Z + \frac{1}{c} (v_1 M - v_2 L) \right] \end{aligned} \right\},$$

(v_1, v_2, v_3) being the components of the velocity with which the charge moves.

The rate at which work is done is given by the equation

$$\begin{aligned} f_t &= f_x v_1 + f_y v_2 + f_z v_3 \\ &= \rho [X v_1 + Y v_2 + Z v_3]. \end{aligned}$$

In accordance with the ideas of the Principle of Relativity we can write the components of the force-four-vector in the form

$$\left. \begin{aligned} f_0 &= \rho_0 [\quad \quad \quad + f_{12} w_2 + w_3 f_{13} + w_4 f_{14}] \\ f_1 &= \rho_0 [f_{21} w_1 \quad \quad \quad + w_3 f_{23} + w_4 f_{24}] \\ f_2 &= \rho_0 [w_1 f_{31} + w_2 f_{32} \quad \quad \quad + w_4 f_{34}] \\ f_3 &= \rho_0 [w_1 f_{41} + w_2 f_{42} + w_3 f_{43} \quad \quad \quad] \end{aligned} \right\} \dots (1)$$

these equations are obtained by writing¹

$$\begin{aligned} f_{12}, f_{21}, f_{13} &\text{ for } L, M, N, \\ f_{14}, f_{24}, f_{34} &\text{ for } -i(X, Y, Z), \end{aligned}$$

$$\begin{aligned} w_1, w_2, w_3, w_4 &\text{ for } \frac{1}{\sqrt{1-v^2/c^2}} [v_1/c, v_2/c, v_3/c, i], \\ \rho_0 &\text{ for } \rho \sqrt{1-v^2/c^2}. \end{aligned}$$

For finding out the total force on the electron, we have to integrate the above expressions for the force-four-vector over the whole volume of the electron. Supposing that the components of the electric and magnetic force do not vary throughout the volume of the electron, the force-components are obtained by writing simply (e) the invariant charge instead of (ρ_0) in equations (1).

3.

The calculation of the Effective force is a matter of some difficulty. The question is: "If an electron moves with a variable velocity, what are the terms corresponding to the quantities $\left(m \frac{d^2 x}{dt^2}, m \frac{d^2 y}{dt^2}, m \frac{d^2 z}{dt^2}\right)$ in particle dynamics?"

Einstein solves the difficulty by saying that instead of the observer's time dt we have to introduce here the proper time (Eigenzeit) of motion of the electron. This conclusion² is reached in a general way from his theory of the equivalence of the forms for equation of motion of material particles when referred to systems moving with uniform

¹The notation used throughout the paper is that of Minkowski, vide *Math. Ann.* Vol. lxxviii, p. 472 *et seq.* § 12, where this particular theorem occurs in an abbreviated form.

²A. Einstein, *Jahrbuch der Radioaktivität*, Vol. iv. 1907

velocity past each other. Minkowski³ practically uses the same hypothesis as I have done (Effective force is equivalent to the Impressed force), but in case of the electron he begins by implicitly ascribing a rest-mass to the electron. But the method adopted by me is fundamentally different, as will appear in due course. Elsewhere, Minkowski⁴ deduces it from the Principle of Least Action, combined with the principle of conservation of mass in a space perpendicular to the axis of motion. Besides, the investigation has a direct bearing on the theory of Electromagnetic momentum as developed by Lorentz and Abraham.

4.

Let us now concentrate our attention on a single electron moving with a velocity v . The force components at an external point due to the motion of the electron are given by the equations (1). Generalising or rather recasting Maxwell's theorem of stresses into new forms, Minkowski has shown that the force components (f_x, f_y, f_z, f_l) can be put into the forms

$$\left. \begin{aligned} f_x &= \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} + \frac{\partial X_l}{\partial l} \\ f_y &= \frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} + \frac{\partial Y_l}{\partial l} \\ f_z &= \frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} + \frac{\partial Z_l}{\partial l} \\ f_l &= \frac{\partial L_x}{\partial x} + \frac{\partial L_y}{\partial y} + \frac{\partial L_z}{\partial z} + \frac{\partial L_l}{\partial l} \end{aligned} \right\} \quad \dots (2)$$

$$\left. \begin{aligned} \text{where } X_x &= \frac{1}{8\pi} [f_{23}^2 + f_{34}^2 + f_{42}^2 - f_{12}^2 - f_{13}^2 - f_{14}^2] \\ X_y &= \frac{1}{4\pi} [f_{13}f_{32} + f_{14}f_{42}] \end{aligned} \right\} \quad \dots (3)$$

The theorem is proved by substituting, in equations (1), the values of $\rho_0 w_1, \rho_0 w_2, \rho_0 w_3, \rho_0 w_4$ obtained from the fundamental equation

$$\text{lor } f = 4\pi\rho_0(w_1, w_2, w_3, w_4)$$

and effecting the necessary transformations with the aid of the second fundamental equation

$$\text{lor } f = 0.^5$$

In the present case, the field is due to a single moving charge. The quantities [$X_x, X_y, \dots$] can be easily calculated from the Potential four-vector $\mathbf{a}$, for the six-vector f is equivalent to curl $\mathbf{a}$.

In a paper⁵ communicated sometime ago to the *Philosophical Magazine*, I have shown that the Potential four-vector $\mathbf{a}$ at an external space-time point (x', y', z', l') due

to the motion of a charge e occupying the point (x, y, z, l) is equivalent to $\frac{ew}{R}$, where

$$w \text{ is velocity four-vector} = \left(\frac{dx}{ds}, \frac{dy}{ds}, \frac{dz}{ds}, \frac{dl}{ds} \right),$$

and R is the perpendicular distance from the external point on the line of motion of the electron. We have

$$R^2 = (x-x')^2 + (y-y')^2 + (z-z')^2 + (l-l')^2 + [(x-x')w_1 + (y-y')w_2 + (z-z')w_3 + (l-l')w_4]^2.$$

We have now

$$\begin{aligned} f_{hk} &= \frac{\partial a_k}{\partial x_h} - \frac{\partial a_h}{\partial x_k} \quad (h, k=1, 2, 3, 4), \\ \therefore f_{12} &= \frac{\partial a_2}{\partial x'} - \frac{\partial a_1}{\partial x'} = \frac{\partial}{\partial x'} \left(\frac{ew_2}{R} \right) - \frac{\partial}{\partial y'} \left(\frac{ew_1}{R} \right) \\ &= e(a_1w_2 - a_2w_1); \end{aligned}$$

where

$$\begin{aligned} a_1 &= \frac{\partial}{\partial x'} \left(\frac{1}{R} \right), \quad a_2 = \frac{\partial}{\partial y'} \left(\frac{1}{R} \right), \quad a_3 = \frac{\partial}{\partial z'} \left(\frac{1}{R} \right), \\ a_4 &= \frac{\partial}{\partial l'} \left(\frac{1}{R} \right). \end{aligned}$$

Therefore we have

$$\begin{aligned} X_x &= \frac{e^2}{8\pi} [(a_2w_3 - a_3w_2)^2 + (a_3w_4 - a_4w_3)^2 + (a_4w_2 - a_2w_4)^2 \\ &\quad - (a_1w_2 - a_2w_1)^2 - (a_1w_3 - a_3w_1)^2 - (a_1w_4 - a_4w_1)^2]. \end{aligned}$$

Now putting $a^2 = a_1^2 + a_2^2 + a_3^2 + a_4^2$

and using the identity

$$a_1w_1 + a_2w_2 + a_3w_3 + a_4w_4 = 0,$$

we easily prove that

$$X_x = \frac{e^2}{8\pi} [-a^2(1 + 2w_1^2) + 2a_1^2].$$

Similarly

$$X_y = \frac{e^2}{8\pi} [-a^2(1 + 2w_2^2) + 2a_2^2],$$

$$X_z = \frac{e^2}{4\pi} [-w_1w_2a^2 + a_1a_2], \text{ \&c.}$$

We shall now calculate the total force on the space exterior to the electron. According to the Principle of Relativity, this space must be uniquely defined. In our case, this space is perpendicular to the axis of motion of the electron, and is bounded on the inside by the surface of the electron. The external boundary is at an infinite distance. Let $d\Omega$ denote an element of volume of this space. Then the total force is given by

$$F_x = \int f_x d\Omega = \int \left[\frac{\partial X_x}{\partial x'} + \frac{\partial X_y}{\partial y'} + \frac{\partial X_z}{\partial z'} + \frac{\partial X_l}{\partial l'} \right] d\Omega \quad (4)$$

Now since a , and consequently $f_{12}, f_{23}, \dots, f_{41}, \dots$, are functions of the relative distance $[(x-x'), (y-y'), (z-z'), (l-l')]$,

we have

$$\frac{\partial X_x}{\partial x'} = -\frac{\partial X_x}{\partial x},$$

³H. Minkowski, "Raum und Zeit," § iv. *Phys. Zeit.*, 1911.

⁴H. Minkowski, *Math. Ann.*, vol. lxxviii. Appendix.

⁵It seems to have escaped the notice of investigators on this particular subject that the Potential four-vector in the form given by me is implicitly contained in a statement of Minkowski's ("Raum und Zeit," §5). The passage came to my notice only recently when I was making a critical study of Minkowski's works.

Therefore

$$F_x = - \left[\frac{\partial}{\partial x} \int Xx d\Omega + \frac{\partial}{\partial y} \int Xy d\Omega + \frac{\partial}{\partial z} \int Xz d\Omega + \frac{\partial}{\partial l} \int Xl d\Omega \right].$$

Now

$$\int Xx d\Omega = \frac{e^2}{8\pi} \int \left[-a^2 (1 + 2\omega_1^2) + 2a_1^2 \right] d\Omega,$$

$$\int Xy d\Omega = \frac{e^2}{4\pi} \int \left[-\omega_1\omega_2 a^2 + a_1 a_2 \right] d\Omega, \text{ \&c.}$$

We have now to calculate the value of the integrals

$$\int a_1^2 d\Omega, \int a_2^2 d\Omega, \int a_1 a_2 d\Omega, \text{ \&c.}$$

We have

$$a_1 = \frac{\partial}{\partial x'} \left(\frac{1}{R} \right) = \frac{1}{R^3} \left[(x-x') + \omega_1 \left\{ (x-x')\omega_1 + (y-y')\omega_2 + (z-z')\omega_3 + (l-l')\omega_4 \right\} \right].$$

Now let us introduce a Lorentz-transformation by means of which the axis of motion becomes the new time-axis. Let (ξ, η, ζ, ν) denote the new coordinates. We have then

$$\begin{bmatrix} (\xi - \xi') \\ (\eta - \eta') \\ (\zeta - \zeta') \\ (\nu - \nu') \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \end{bmatrix} \begin{bmatrix} x - x' \\ y - y' \\ z - z' \\ l - l' \end{bmatrix},$$

$$\text{where } A_{1k}^2 + A_{2k}^2 + A_{3k}^2 + A_{4k}^2 = 1 \text{ and } A_{1h}A_{1k} + A_{2h}A_{2k} + A_{3h}A_{3k} + A_{4h}A_{4k} = 0 \left. \vphantom{\begin{matrix} A_{1k}^2 + A_{2k}^2 + A_{3k}^2 + A_{4k}^2 = 1 \\ A_{1h}A_{1k} + A_{2h}A_{2k} + A_{3h}A_{3k} + A_{4h}A_{4k} = 0 \end{matrix}} \right\}.$$

Since the line of motion is the new time-axis, we have

$$(\nu - \nu') = i[\omega_1(x - x') + \omega_2(y - y') + \omega_3(z - z') + \omega_4(l - l')];$$

we have therefore

$$A_{41} = i\omega_1, \quad A_{42} = i\omega_2, \quad A_{43} = i\omega_3, \quad A_{44} = i\omega_4.$$

Now using the above transformation, we have

$$R^2 = (\xi - \xi')^2 + (\eta - \eta')^2 + (\zeta - \zeta')^2$$

and

$$\begin{aligned} (x - x') + \omega_1[(x - x')\omega_1 + (y - y')\omega_2 + (z - z')\omega_3 + (l - l')\omega_4] \\ = A_{11}(\xi - \xi') + A_{21}(\eta - \eta') + A_{31}(\zeta - \zeta') + A_{41}(\nu - \nu') - i\omega_1(\nu - \nu') \\ = A_{11}(\xi - \xi') + A_{21}(\eta - \eta') + A_{31}(\zeta - \zeta'), \text{ for } A_{41} = i\omega_1. \end{aligned}$$

Then

$$\begin{aligned} \int a^2 d\Omega &= A_{11}^2 \int \frac{(\xi - \xi')^2}{R^6} d\Omega + A_{21}^2 \int \frac{(\eta - \eta')^2}{R^6} d\Omega \\ &+ A_{31}^2 \int \frac{(\zeta - \zeta')^2}{R^6} d\Omega + 2A_{11}A_{21} \int \frac{(\xi - \xi')(\eta - \eta')}{R^6} d\Omega + \dots \end{aligned}$$

Now we have, since the integration extends over the space internally bounded by the sphere

$$(\xi - \xi_0)^2 + (\eta - \eta_0)^2 + (\zeta - \zeta_0)^2 = a^2,$$

$$\int \frac{(\xi - \xi')^2}{R^6} d\Omega = \int \frac{(\eta - \eta')^2}{R^6} d\Omega = \int \frac{(\zeta - \zeta')^2}{R^6} d\Omega = \frac{1}{3} \int \frac{d\Omega}{R^4},$$

and from symmetry,

$$\int \frac{(\xi - \xi')(\eta - \eta')}{R^6} d\Omega = 0.$$

Now we have

$$\int \frac{d\Omega}{R^4} = -\frac{4\pi}{a},$$

$$\therefore \int a_1^2 d\Omega = -\frac{4\pi}{3a} [A_{11}^2 + A_{21}^2 + A_{31}^2] = -\frac{4\pi}{3a} (1 + \omega_1^2),$$

and

$$\begin{aligned} \int a_1 a_2 d\Omega &= -\frac{4\pi}{3a} [A_{11}A_{21} + A_{12}A_{22} + A_{13}A_{23}] \\ &= -\frac{4\pi}{3a} [A_{14}A_{24}] = -\frac{4\pi}{3a} \omega_1 \omega_2. \end{aligned}$$

$$\begin{aligned} \therefore X_x &= -\frac{e^2}{8\pi} \left[-\frac{4\pi}{a} (1 + 2\omega_1^2) + 2 \cdot \frac{4\pi}{3a} (1 + \omega_1^2) \right] \\ &= \frac{2e^2}{3a} (\frac{1}{2} + \omega_1^2), \end{aligned}$$

$$\text{and } X_y = -\frac{e^2}{4\pi} \left[-\omega_1\omega_2 \cdot \frac{4\pi}{a} + \frac{4\pi}{3a} \omega_1\omega_2 \right] = \frac{2e^2}{3a} \omega_1\omega_2.$$

Then we have similarly

$$\left. \begin{aligned} Y_y &= \frac{2e^2}{3a} (\frac{1}{2} + \omega_2^2), & Z_z &= \frac{2e^2}{3a} (\frac{1}{2} + \omega_3^2), \\ L_l &= \frac{2e^2}{3a} (\frac{1}{2} + \omega_4^2), & X_l &= \frac{2e^2}{3a} \omega_1\omega_4, \text{ \&c.} \end{aligned} \right\} (5)$$

Now we have

$$\begin{aligned} F_x &= -\frac{2e^2}{3a} \left[\frac{\partial}{\partial x} (\frac{1}{2} + \omega_1^2) + \frac{\partial}{\partial y} (\omega_1\omega_2) + \frac{\partial}{\partial z} (\omega_1\omega_3) \right. \\ &\quad \left. + \frac{\partial}{\partial l} (\omega_1\omega_4) \right], \end{aligned}$$

i.e.

$$\begin{aligned} F_x &= -\frac{2e^2}{3a} \left[\left(\omega_1 \frac{\partial}{\partial x} + \omega_2 \frac{\partial}{\partial y} + \omega_3 \frac{\partial}{\partial z} + \omega_4 \frac{\partial}{\partial l} \right) \omega_1 + \right. \\ &\quad \left. \omega_1 \left(\frac{\partial \omega_1}{\partial x} + \frac{\partial \omega_2}{\partial y} + \frac{\partial \omega_3}{\partial z} + \frac{\partial \omega_4}{\partial l} \right) \right]. \end{aligned}$$

The second term = 0 from the condition $\text{Div } \mathbf{a} = 0$, for this gives

$$\frac{\partial}{\partial x} \left(\frac{e\omega_1}{R} \right) + \frac{\partial}{\partial y} \left(\frac{e\omega_2}{R} \right) + \frac{\partial}{\partial z} \left(\frac{e\omega_3}{R} \right) + \frac{\partial}{\partial l} \left(\frac{e\omega_4}{R} \right) = 0,$$

$$\text{i.e. } \frac{1}{R} \text{Div } \omega + (\omega_1 a_1 + \omega_2 a_2 + \omega_3 a_3 + \omega_4 a_4) = 0,$$

from which $\text{Div } \omega = 0$, for the last term is identically zero.

The X -component of the force on the external space

$$= -\frac{2e^2}{3a} \frac{d^2 x}{ds^2}, \text{ for } \frac{d}{ds} = \omega_1 \frac{\partial}{\partial x} + \omega_2 \frac{\partial}{\partial y} + \omega_3 \frac{\partial}{\partial z} + \omega_4 \frac{\partial}{\partial l} \quad (6)$$

We may interpret this force as the reaction of the electron on the external space, which is supposed for purposes of substantiation to be composed of aether. The effective force on the electron is equal and opposite to this force,

and has therefore the components

$$\frac{2e^2}{3a} \frac{d^2x}{ds^2}, \frac{2e^2}{3a} \frac{d^2y}{ds^2}, \frac{2e^2}{3a} \frac{d^2z}{ds^2}, \frac{2e^2}{3a} \frac{d^2l}{ds^2},$$

(N.B.—We have for small velocities $ds=c dt$ approximately,

$$\therefore \frac{2e^2}{3a} \frac{d^2x}{ds^2} = \frac{2e^2}{3ac^2} \frac{d^2x}{dt^2}, \text{ \&c.}$$

We therefore observe that the quantity $\frac{2e^2}{3ac^2}$ plays here the same part as the mass m_0 . We can therefore call $\frac{2e^2}{3ac^2}$ the rest-mass of the electron, and put it equivalent to m_0 .

5.

Now a few remarks on the equations (2). These were first introduced into Mathematical Physics by Maxwell about 1865. Ever since their introduction, various efforts have been made by different investigators for getting something out of them, and in certain cases they have yielded very valuable information, and led to many important results. We may cite for example, Maxwell's prediction of the existence of Radiation Pressure. The close analogy of the equations (2) with the equations of elasticity led Maxwell to propose his famous theory of "Stresses," i.e. to imagine that the electric forces are due to a distribution of the stresses ($Xx, Xy \dots$) in aether, which behaves in this case like an elastic solid. But this theory is fraught with many difficulties, which have been pointed out from time to time by several investigators⁶. In a paper⁷ communicated to the *Phil. Mag.*, the author observed that though the forces can be well accounted for, the Energy of Electrification cannot be accounted for on Maxwell's hypothesis.

Another direction in which the equations (2) have been exploited is the subject of Electromagnetic mass of an electron. When an electron moves with a certain velocity, it creates round it an electric as well as a magnetic field. We can say with Maxwell that the energy is stored in the aether, and the electron by its motions exerts a force on every particle of aether.

If we now integrate this force over the whole space⁸ exterior to the electron, the first three terms involving $\left(\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}\right)$ can be reduced to a surface-integral. The bounding surface is taken to be at an infinite distance, thereby the surface integrals are made to vanish. The total force on the aether thus comes out in the form

$$\frac{dM}{dt} = \frac{1}{lc} \frac{\partial M}{\partial t}.$$

Now assuming that the force exerted by the aether on the electron is equal and opposite to the force exerted by the electron on the aether, the reaction of aether on the electron becomes equivalent to $-\frac{1}{lc} \frac{\partial M}{\partial t}$. In analogy with Classical

Mechanics, we can call $\left(\frac{iM}{c}\right)$ a momentum.

This is, in brief, the theory of Electromagnetic momentum as developed by Abraham, Lorentz⁹, and others. We do not enter into a discussion of the rival theories of Lorentz and Abraham on the shape of the electron during motion. The electromagnetic mass is obtained from either of the relations $m_t = \frac{iM}{cv}$ and $m_l = i \frac{\partial M}{c \partial v}$, m_t and m_l denoting respectively the transverse and longitudinal masses of the electron.

But several objections can be raised to this theory of Electromagnetic momentum. In the first place, the integration is extended over the space of the observer, whereas the Principle of Relativity requires that it should be extended over the space perpendicular to the axis of motion of the electron, and external to the volume occupied by the electron. This is what I have done in the foregoing, and I believe that this is quite in keeping with Minkowski's ideas of equivalence of time and space. Secondly, the volume of integration is supposed to be bounded by a sphere at an infinite distance only, and no notice is taken of the internal boundary which must coincide with the surface of the electron. In fact, it looks as if the surface integrals had to go, because the authors wanted to get rid of them.

In the theory proposed by me, I have refrained from putting any interpretation on the quantities ($X_x, X_y, \dots$). Taking the theorem as it is, the total effective force on the aether has been obtained by integrating f over the whole space perpendicular to the axis of motion of the electron, the space being bounded on the inside by the surface of the electron. The "Effective force" on the electron has been taken to be equal and opposite to this force.

I may be allowed to point out here that this procedure by no means confers substantiality upon the aether. It is a fictitious creation, introduced for the sake of arriving at a result which, from its very nature, can be attempted only by indirect means.

It is remarkable that none of the quantities $\int X_x d\Omega$, & c. vanish in this case, as in the other theories. The "Effective" force on an electron, instead of simply being the rate of change of "Momentum" becomes the sum total of the time-rate of change of the quantity $\int \frac{\partial X_l}{\partial t} d\Omega$ plus the space-rates of changes of the quantities $\int \frac{\partial X_x}{\partial x} d\Omega, \int \frac{\partial X_y}{\partial y} d\Omega, \dots$

⁶Maxwell, 'Electricity and Magnetism', third edition, Vol. i, chap. v, footnote p. 165.

⁷*Phil. Mag.*, March 1917.

⁸N. B. This space is the absolute space of the Pre-Relativity Period.

⁹Lorentz, 'Theory of Electrons', chap. 1, § 26 et seq.

These latter quantities involve "velocity" in the second order, whereas $\int \frac{\partial X_i}{\partial t} d\Omega$ involves "velocity" in the first order, so that when the velocity is a small fraction of the velocity of light, the theorem approximates to Newton's Second Law of Motion.

The rest-mass calculated on this basis is equivalent to $\frac{1}{2} \cdot \frac{e^2}{ac^2}$ and as such coincides with the value obtained by Sir J. J. Thomson for slow-moving electrons, and with

that obtained by Lorentz and Einstein. The variation of mass with velocity is determined by the Principle of Relativity as in the theories of Lorentz and Einstein.

In conclusion, I wish to express my thanks to my friend and colleague Mr. Satyendra Nath Basu, M.Sc., for much help and useful criticism.

Calcutta University College of Science,
Physical Dept., July 10, 1917.

6. ON THE INFLUENCE OF THE FINITE VOLUME OF MOLECULES ON THE EQUATION OF STATE*

M. N. SAHA & S. N. BASU

(*Phil. Mag.*, *Sr. VI*, **36**, 199, 1918)

It is well known that the departure of the actual behaviour of gases from the ideal state defined by the equation $p = \frac{NK\theta}{v}$ is due to two causes: (1) the finiteness of the volume of the molecules, (2) the influence of the forces of cohesion, i.e., the attractive forces amongst the molecules. van der Waals was the first to deduce an equation of state in which all these factors are taken into account; according to van der Waals, we have

$$p = \frac{NK\theta}{v-b} - \frac{a}{v^2} \quad (1)$$

where $b = 4 \times$ volume of the molecules, a defines the forces of cohesion.

In all subsequent modifications of this equation (Clausius, Dieterici, or D. Berthelot), the changes which have been proposed all relate to the influence of the cohesive forces; the part of the argument dealing with the finiteness of molecular volumes is generally left untouched.

But it has been found that the results of experiments do not agree with the predictions of theory if we regard a and b as absolute constants. Accordingly it has been proposed to regard both a and b as functions of volume and temperature.¹

But before proceeding to these considerations, it is necessary to scrutinize whether the influence of finite molecular volumes is properly represented by the term b . From theoretical considerations, the conclusion has been reached that this is not the case. The argument is as follows: According to Boltzmann's theory,

the entropy $S = K \log W + C$,

where K = Boltzmann's gas constant, W = probability of the state. Let us now calculate the probability that a number of N molecules originally confined within the volume V_0 and possessing finite volumes, shall be contained in a volume V . Neglecting the influence of internal forces, the probability for the first molecule is $\frac{V}{V_0}$, for the second mole-

cule the probability is $\frac{V-\beta}{V_0-\beta}$, where $\beta = 8 \times$ volume of a single molecule, for when the first molecule is in position, the space enclosed by a concentric sphere of double the radius of the molecule will not be available for the second molecule. The available space is therefore $V-\beta$, whence the probability is $\frac{V-\beta}{V_0-\beta}$. Introducing similar considerations

for the rest of the molecules, we have

$$W = \frac{V}{V_0} \cdot \frac{V-\beta}{V_0-\beta} \cdot \frac{V-2\beta}{V_0-2\beta} \cdots \frac{V-(N-1)\beta}{V_0-(N-1)\beta} \quad (2)$$

We are, of course, neglecting those cases in which partial overlapping of the regions occupied by two or more molecules occurs; for the number of such cases can at best be a small fraction of the total number. Even cases of actual association do not include these, for in that case, two discrete molecules become merged into one, without their outer surfaces being actually in contact.

From the relations $S = K \log W + C$

$$\text{and} \quad \left(\frac{\partial S}{\partial V} \right)_u = \frac{p}{\theta}$$

we can easily verify that

$$\begin{aligned} p &= - \frac{K\theta}{\beta} \log \frac{V-n\beta}{V} \\ &= - \frac{R\theta}{2b} \log \frac{V-2b}{V} \quad (R = NK) \end{aligned} \quad (3)$$

*Communicated by the Authors.

¹Compare van der Waals, *Proc. Amst.*, 1916; Van Laar, *Proc. Amst.*, vol. xvi, p. 44.

As a first approximation, when b is small compared to v , we obtain $p = \frac{NK\theta}{v}$ (Boyle-Charles-Avogadro Law), and as a second approximation we obtain

$$p = \frac{NK\theta}{v-b} \quad (\text{van der Waals correction}).$$

We also note that

$$pV = NK\theta \cdot \frac{x}{1-e^{-x}}, \text{ where } x = \frac{\beta p}{K\theta} \quad (4)$$

To account for the influence of internal forces, we multiply, following the lead of Dieterici, the above expression (3) by $e^{-\frac{a}{NK\theta v}}$, a having the same significance as before.

From this equation of state, we can easily verify the following results for the critical point:

$$\text{Critical volume, } V_c = \frac{2e}{e-1} b = 3.166b,$$

$$K = \frac{NK\theta_c}{p_c V_c} = 3.513,$$

The corresponding values of V_c from the van der Waals and the Dieterici equations are $(3b, 2b)$ respectively, and of K are $\left(\frac{8}{3} = 2.66, \frac{e^2}{2} = 3.695\right)$ respectively.

As a matter of fact, for the simpler gases, the value of ' K ' obtained in this paper agrees better with the experimental results than the Dieterici value $\frac{e^2}{2}$; we have for oxygen² $K=3.346$, for nitrogen³ $K=3.53$, for argon⁴ $K=3.424$, for xenon⁵ $K=3.605$. We need not consider the van der Waals value $\frac{8}{3}$, for it fails entirely.

²Mathias and K. Onnes, *Proc. Amst.*, Feb. 1911.

³Berthelot, *Bull. de la Soc. France de Phys.*, 167 (1901).

⁴Mathias, Onnes, and Crommelin, *Proc. Amst.*, 1913, p. 960, vol. xv.

⁵Paterson, Cripps, Whytlaw-Gray, *Proc. Roy. Soc. Lond. A*, lxxvi, p. 579 (1912).

The most serious drawback to Dieterici's equation is, according to Prof. Lewis (*vide* Lewis's Physical Chemistry, vol. ii. p. 117) that it makes b or the limiting volume $= \frac{V_c}{2}$, while the limiting volume, obtained by the extrapolation of Cailletet-Mathias mean density line to the temperature $\theta = 0^\circ K$ is about $\frac{V_c}{4}$. The value of b obtained in this paper, viz., $\frac{V_c}{3.16}$ therefore agrees better with this value.

It is yet premature to predict what influence this investigation will have on the speculations concerning the variability of the volume of molecules with temperature. A more detailed investigation dwelling upon this point, and the application of the formula (4) to Amagat's (pv, p) curves, will be communicated shortly. Meanwhile we point out

that the factor $e^{-\frac{a}{NK\theta v}}$ has been introduced into the expression for ' p ' only as a provisional measure, though it is considered that this step, though not quite exact, is one in the right direction. In the next paper an attempt will be made to introduce energy into probability calculations.

Sir T. N. Palit Laboratory of Science, Calcutta.

Note added in proof.—On consulting the literature on the subject, we noticed that in several papers in the Amsterdam Proceedings (*vide* vol. xv. p. 240 *et seq.*), Dr. Keesom of Leyden had also made attempts to deduce the equation of state from Boltzmann's entropy principle. But, in the expression (2) for W , he introduces, before differentiation, an approximation in which terms up to second order in b/v are retained only. In this way, he arrives at the van der Waals' form $v-b$ for the influence of finite molecular volumes. In obtaining our present equation of states (4), no such approximation has been made.

7. ON THE MECHANICAL AND ELECTRODYNAMICAL PROPERTIES OF THE ELECTRON

(*Phys. Rev.*, 13, 34, 1919)

The object of the present paper is to extend Minkowski's method¹ of four-dimensional analysis to the investigation of the mechanical and electrodynamical problems connected

with the electron. As is well known, Minkowski's four dimensional analysis is based on the principle of relativity, and we have thereby to abandon two time-honored concepts of physics, i.e., absolute independence of time and space, and the constancy of mass. The correctness of these two principles is no longer a matter of hypothesis, but is founded on experiments. It is therefore to be hoped

¹Minkowski's method of four-dimensional analysis is expounded in two papers: (1) *Raum und Zeit*, published in the *Phys. Zeits.*, and (2) *Die Grundgleichungen für die Electro-magnetischen Vorgänge in bewegten Körpern*—*Gött. Nach.*, 1908. These two papers have been translated by me, and are being published by the Calcutta University.

that the results of these investigations will be helpful to us for the elucidation of the mechanical and electrical problems connected with the electron, though sometimes difficulty may be encountered in putting proper interpretation on these results.

The notation is the same as that adopted by Minkowski and for the convenience of the reader, it is explained at the very outset.

$(x, y, z, t \pm iet)$ denotes the space and time coordinates of any point in the four-dimensional world

$$(u_1, u_2, u_3, u_4) = \frac{1}{\sqrt{1 - \frac{u^2}{c^2}}} \left[\frac{u_1}{c}, \frac{u_2}{c}, \frac{u_3}{c}, i \right]$$

denotes the velocity four-vector of the point

$$\text{We put } ds^2 = -(dx^2 + dy^2 + dz^2 + d\tau^2)$$

therefore we have

$$(x_1, x_2, x_3, x_4) = \left(\frac{dx}{ds}, \frac{dy}{ds}, \frac{dz}{ds}, \frac{d\tau}{ds} \right),$$

$$\text{and } \sqrt{-1} (x_1, x_2, x_3, x_4)$$

denote the direction cosines of the four-dimensional tangent to the path of the particle. c = velocity of light in space.

$$\text{We put } (f_{23}, f_{31}, f_{12}) = (H_x, H_y, H_z),$$

the components of the magnetic field, and

$$(f_{14}, f_{24}, f_{34}) = -i [E_x, E_y, E_z],$$

the components of the electric field. Minkowski has shown that f constitutes a six-vector.

$$(a_1, a_2, a_3, a_4) = [F, G, H, i\phi],$$

are the components of the potential four-vector; (F, G, H) are the vector potentials, ϕ is the scalar potential.

ρ = electrical space-density;

$$\rho \left[\frac{u_1}{c}, \frac{u_2}{c}, \frac{u_3}{c}, i \right] = \rho_0 (x_1, x_2, x_3, x_4)$$

are the components of the stream four-vectors;

$$\rho_0 = \rho \sqrt{1 - \frac{u^2}{c^2}}$$

is known as the rest-density of electricity.

The vector operator

$$\square = \left(i \frac{\partial}{\partial x} - j \frac{\partial}{\partial y} - k \frac{\partial}{\partial z} - \frac{\partial}{\partial t} \right),$$

is known as the *lor* and the scalar operator

$$\square^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\partial^2}{\partial t^2} \right)$$

is known as the generalised D'Alembertian.

The equations of electrodynamics can be written in the forms

$$\text{lor } f = r,$$

$$f = \text{Curl } a;$$

$$\text{lor } f^* = 0$$

$$\square^2 a = -r,$$

$$\square a = 0.$$

2. The Scalar and Vector Potentials of a Moving Electron.

Lienard,² and almost simultaneously Wiechert³ showed that the scalar and vector potentials are given by the expressions

$$\phi = \frac{e}{r \left(1 - \frac{u}{c} \right)}, \quad (F, G, H) = - \frac{e (u_1, u_2, u_3)}{r \left(1 - \frac{u}{c} \right)},$$

If P be the point at which the potentials are calculated at the time t and M be the position of the electron at the time t_0 where $MP = r(t - t_0)$, the distance MP is denoted by r and $[u]$ denotes the velocity in the position M , and u its component in the direction of r .

The formulae are deduced from the theory of retarded potential and do not involve the principle of relativity.

Several investigators⁴ have shown that the formulae can also be deduced from the theory of relativity and can be thrown into the compact form

$$a = \frac{d[\omega]}{[R\omega]}$$

R being the four-vector joining the two points, $[R\omega]$ denoting the scalar product of R and ω .

It is quite clear that the forms (1) and (2) are quite equivalent.

In a paper published elsewhere, it has been shown that from Minkowski's four-dimensional analysis we obtain

$$a = \frac{d[\omega]}{P}$$

In this formula, (x, y, z, t) denote the time-space coordinates of the electron (A) , (u_1, u_2, u_3, u_4) its velocity components, (x', y', z', t') denote the space-time coordinates of the point B at which the potentials are estimated.

P denotes the four-dimensional perpendicular distance of B from the axis of motion of (A) ; since the direction cosines of this axis are $-i(\omega_1, \omega_2, \omega_3, \omega_4)$, we have

$$\begin{aligned} P^2 &= (x-x')^2 + (y-y')^2 + (z-z')^2 + (t-t')^2 + [(x-x')\omega_1 \\ &\quad + (y-y')\omega_2 + (z-z')\omega_3 + (t-t')\omega_4]^2 \\ &= R^2 + [R\omega]^2. \end{aligned}$$

Now if we make the assumption that the time coordinates are so chosen that

$$R^2 = (x-x')^2 + (y-y')^2 + (z-z')^2 - (t-t')^2 = 0$$

$$\text{i.e., } c^2(t-t')^2 = r^2,$$

$$\text{i.e., } c(t-t') = r,$$

the formula (3) becomes the same as (2) and therefore (1). Also the assumption which we make here about the interval between the time coordinates is identical with the premise of Lienard and Wiechert.

I am not quite certain whether this assumption (4)

²Lienard, *L'éclairage électrique*, 16 (1898), pp. 3, 38 and 106.

³Wiechert, *Arch. Neerl.*, 2, 5 (1900).

⁴Sommerfeld, *Über die Relativitätstheorie*, *Ann. d. Physik*, Vol. 32 & 33.

which is made here is at all essential. I am inclined to think that it is not essential, but necessary only for the interpretation of the result to those three-dimensional beings whose senses are not sharpened enough to enable them to grasp a result expressed in four-dimensional figures.

3. The Electric and Magnetic Fields due to a Moving Electron.

If a denote the potential four-vector, the components of the six-vector f giving the electric and magnetic fields are given by

$$f = \text{Curl } a = \begin{vmatrix} \frac{\partial}{\partial x'} & \frac{\partial}{\partial y'} & \frac{\partial}{\partial z'} & \frac{\partial}{\partial t'} \\ a_1 & a_2 & a_3 & a_4 \end{vmatrix}.$$

Thus $f_{12} = \frac{\partial a_2}{\partial x'} - \frac{\partial a_1}{\partial y'} = \frac{e}{P^3} [\omega_3 \alpha_2 - \omega_2 \alpha_3]$, etc. (5)

where $\alpha_1 = P \frac{\partial P}{\partial x'}$, $\alpha_2 = P \frac{\partial P}{\partial y'}$, ... etc.

we can easily verify that if we put $c(t-t') = r$, we have

$$H_z = \frac{e\beta^2}{r^3\lambda^3} \left[\frac{u_2}{c} (z-z') - \frac{u_3}{c} (y-y') \right],$$

where $\lambda = \left(1 - \frac{Ur}{c}\right)$,

$$= \frac{e\beta^2}{r^3\lambda^3} [u \times r]. \quad (6)$$

The electric forces are given by

$$\begin{aligned} f_{14} &= -iE_x = \frac{\partial a_4}{\partial x'} - \frac{\partial a_1}{\partial t'}, \\ &= \frac{e}{P^3} [\omega_1 (t-t') - \omega_4 (x-x')], \\ &= -i \frac{e\beta^2}{r^3\lambda^3} \left[r \frac{u_1}{c} - (x-x') \right], \end{aligned} \quad (7)$$

and generally

$$E_x = \frac{e\beta^2}{r^3\lambda^3} \left[(x-x') - \frac{ru_1}{c} \right], \quad E = \frac{e\beta^2}{r^3\lambda^3} \left[r - \frac{ru}{c} \right].$$

These values are widely different and simpler than the values obtained from the older theories, for example, compare the values given by Crehore⁵.

The discrepancy is due to the fact that in these older theories, we always assume that the equation

$$(x-x')^2 + (y-y')^2 + (z-z')^2 + (t-t')^2 = 0,$$

is an essential condition. But in performing differentiations with regard to (x', y', z', t') we here assume that they are quite independent of (x, y, z, t) . I am not quite definite as to which of these two standpoints is correct but I am inclined to think that my standpoint is more in accordance with Minkowski's ideas of time and space. However it is preferable to keep an open mind on this point.

4. Maxwell's Stresses, Poynting-Vector, Etc.

Minkowski has shown that if we multiply f by its own matrix, we obtain a matrix

$$ff = \begin{vmatrix} S_{11}-L^2 & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22}-L^2 & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33}-L^2 & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44}-L^2 \end{vmatrix}$$

where $S_{11} = \frac{1}{2} [f_{23}^2 + f_{34}^2 + f_{42}^2 - f_{12}^2 - f_{13}^2 - f_{14}^2]$,

$$S_{12} = [f_{13}f_{32} + f_{14}f_{42}],$$

$$L = \frac{1}{2} [f_{23}^2 + f_{32}^2 + f_{12}^2 + f_{14}^2 + f_{24}^2 + f_{34}^2],$$

and the matrix

$$\frac{1}{4\pi} \begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{vmatrix} = \begin{vmatrix} X_x & X_y & X_z \\ Y_x & Y_y & Y_z \\ Z_x & Z_y & Z_z \end{vmatrix}$$

denote the Maxwellian stresses, i (S_{14} , S_{24} , S_{34}) denote the components of the Poynting-vector, and S_{44} is the energy function. We have generally

$$\begin{aligned} X_x &= \frac{1}{8\pi} [f_{23}^2 + f_{34}^2 + f_{42}^2 - f_{12}^2 - f_{13}^2 - f_{14}^2], \\ X_y &= \frac{1}{4\pi} [f_{13}f_{32} + f_{14}f_{42}], \text{ etc.} \end{aligned} \quad (8)$$

Now on the standpoint taken up by me, it is quite easy to calculate these quantities. It can be shown that

$$X_x = \frac{e^2}{8\pi P^2} [-P^2 (1 + 2\omega_1^2) + \alpha_1^2], \quad X_y = \frac{e^2}{8\pi P^6} [-\omega_1\omega_2 P^2 + \alpha_1\alpha_2]. \quad (9)$$

The Poynting-Vector

$$(X_1, Y_1, Z_1) = \frac{e^3}{8\pi P^6} [(-\omega_1\omega_4 P^2 + \alpha_1\alpha_4), (-\omega_2\omega_4 P^2 + \alpha_2\alpha_4), (-\omega_3\omega_4 P^2 + \alpha_3\alpha_4)]$$

and the energy function

$$S_{44} = L = \frac{e^2}{8\pi P^6} [-P^2 (1 + 2\omega_4^2) + \alpha_4^2]$$

where $\alpha_1 = P \frac{\partial P}{\partial x'}$, $\alpha_2 = P \frac{\partial P}{\partial y'}$, etc.

and $\alpha^2 = \alpha_1^2 + \alpha_2^2 + \alpha_3^2 + \alpha_4^2 = P^2$.

5. The Law of Attraction between Two Moving Electrons.

We can now proceed to find out the attraction which one moving electron exerts upon another moving electron.

According to Lorentz's theorem the components of the force acting on an electron (A) moving in any electromagnetic field are

$$\begin{aligned} X &= e [w_2 f_{12} + w_3 f_{13} + w_4 f_{14}], \\ Y &= e [w_1 f_{21} + w_3 f_{23} + w_4 f_{24}], \\ Z &= e [w_1 f_{31} + w_2 f_{32} + w_3 f_{34}], \end{aligned} \quad (10)$$

and we can also add the fourth or the time component

$$L = -\frac{ie}{c} [X u_1 + Y u_2 + Z u_3], \quad \beta = \sqrt{1 - \frac{v^2}{c^2}}$$

⁵Phys. Rev., July, 1917, p. 448.

which is proportional to the rate at which work is done by the moving charge,—we have

$$L = e[w_1 f_{41} + w_2 f_{42} + w_3 f_{43}].$$

In this case, the field is due to the second electron (charge e' , position $x'y'z'l'$, velocity components $w_1' w_2' w_3' w_4'$).

According to the last section, the potential four-vector

$$a = \frac{e'[w']}{P'}, \text{ where } P'^2 = R^2 + [Rw']^2.$$

We have now, since $f = \text{Curl } a$,

$$\begin{aligned} X &= ee' \left[w_2 \left\{ \frac{\partial}{\partial x} \left(\frac{w_2'}{P'} \right) - \frac{\partial}{\partial y} \left(\frac{w_1'}{P'} \right) \right\} + w_3 \left\{ \frac{\partial}{\partial x} \left(\frac{w_3'}{P'} \right) - \frac{\partial}{\partial z} \left(\frac{w_1'}{P'} \right) \right\} + w_4 \left\{ \frac{\partial}{\partial x} \left(\frac{w_4'}{P'} \right) - \frac{\partial}{\partial l} \left(\frac{w_1'}{P'} \right) \right\} \right] \\ &= ee' \left[\frac{\partial}{\partial x} \left(\frac{w_1 w_1' + w_2 w_2' + w_3 w_3' + w_4 w_4'}{P'} \right) - \left(w_1 \frac{\partial}{\partial x} + w_2 \frac{\partial}{\partial y} + w_3 \frac{\partial}{\partial z} + w_4 \frac{\partial}{\partial l} \right) \left(\frac{w_1'}{P'} \right) \right], \end{aligned}$$

Now putting $\Phi = ee' (w_1 w_1' + w_2 w_2' + w_3 w_3' + w_4 w_4') / P'$,

$$\text{we find that } X = \frac{\partial \Phi}{\partial x} - \frac{d}{ds} \left(\frac{\partial \Phi}{\partial x} \right),$$

where $\frac{\partial}{\partial x}$ denotes differentiation in which x is explicitly involved, similarly with

$$\frac{\partial}{\partial w_1} = \frac{\partial}{\partial \frac{dx}{ds}},$$

$$\frac{d}{ds} = \left(w_1 \frac{\partial}{\partial x} + w_2 \frac{\partial}{\partial y} + w_3 \frac{\partial}{\partial z} + w_4 \frac{\partial}{\partial l} \right),$$

as is easily seen. We have similarly

$$\begin{aligned} Y &= \frac{\partial \Phi}{\partial y} - \frac{d}{ds} \left(\frac{\partial \Phi}{\partial y} \right), \quad Z = \frac{\partial \Phi}{\partial z} - \frac{d}{ds} \left(\frac{\partial \Phi}{\partial z} \right), \\ L &= \frac{\partial \Phi}{\partial l} - \frac{d}{ds} \left(\frac{\partial \Phi}{\partial l} \right). \end{aligned} \quad (11)$$

We can say that ϕ is the kinetic-potential of the electron (A) in the field of the electron (B). Similarly if ϕ' denote the Kinetic-potential of the electron (B) in the field of (A),

$$\phi' = ee' (w_1 w_1' + w_2 w_2' + w_3 w_3' + w_4 w_4') / P,$$

$$P^2 = R^2 + (Rw)^2,$$

and we have similarly

$$X' = \frac{\partial \Phi'}{\partial x'} - \frac{d}{ds'} \left(\frac{\partial \Phi'}{\partial x'} \right), \quad (12)$$

Let us now interpret the results in three dimensions. We have

$$X = \frac{ee' \beta'^2}{r^3 \lambda^3 \beta'} (x - x') \left(1 - \frac{uv \cos \theta}{c^2} \right) - \frac{ee' \beta'^2}{r^2 \lambda^3 \beta^3 c} \left(1 - \frac{Ur}{c} \right) u',$$

$$\text{where } \beta = \sqrt{1 - \frac{v^2}{c^2}}, \beta' = \sqrt{1 - \frac{v'^2}{c^2}}, \lambda = \left(1 - \frac{Ur}{c} \right). \quad (13)$$

In three dimensions, the forces are equivalent to a force of repulsion

$$\frac{ee' \beta'^2}{r^3 \lambda^3 \beta} \left(1 - \frac{uv \cos \theta}{c^2} \right) r,$$

in the direction of the line joining the two points, and a force

$$\frac{ee' \beta'^2}{r^2 \lambda^3 \beta^3 c} \left(1 - \frac{Ur}{c} \right) u', \quad (14)$$

in the direction of the velocity of the second or the attracting point.

We thus perceive that the force which comes out in a very simple form in four dimensions takes a very complicated form in three dimensions.

The kinetic potential

$$\phi = \frac{ee' \left(1 - \frac{uv' \cos \theta}{c^2} \right)}{\left(1 - \frac{Ur}{c} \right) \beta}. \quad (15)$$

This kinetic potential is practically coincident with the kinetic potential assumed by Clausius in order to find out the law of attraction between two moving charges of electricity; Clausius has shown that this kinetic potential leads to the celebrated electrodynamic laws of Ampere. A short resumé of the work done in this connection is given below for the purpose of comparison. The problem was first enunciated by Gauss in the year 1835, and was called by him the fundamental keystone of electrodynamics.⁶

(1) Gauss (1835): The forces are the derivatives with regard to (x, y, z) of the potential function,

$$\phi = \frac{ee'}{r} \left(1 - \frac{3}{2c} \frac{d^2 r}{dt^2} \right).$$

(2) Weber (1843) takes the potential function

$$\phi = \frac{ee'}{r} \left(1 - \frac{1}{c^2} \frac{dr^2}{dt} \right).$$

Both of these forms have been long discredited. Later writers have pointed out that the force cannot be simply the derivations with regard to (x, y, z) of some potential function, but are the Lagrangian derivatives of a certain kinetic-potential. We give the form of this kinetic-potential according to different investigators.

(1) Clausius (1881):

$$\phi = \frac{ee'}{r} \left(1 - \frac{uu' \cos \theta}{c^2} \right),$$

where u and u' are the velocities of the two electrons, and θ is the angle between their lines of motion. In two papers communicated to the Crele's journal⁷, Clausius deduces Ampere's law of electrodynamic action between two currents from this law.

⁶For the literature on the subject, see Maxwell, Electricity and Magnetism, Vol 2, chap. XXIII, and J. J. Thomson, Application of Dynamics to Problems of Physics and Chemistry, pp. 35.

⁷Vols. 82 and 83.

(2) J. J. Thomson:

$$\phi = \frac{ee'}{r} \left(1 - \frac{\mu}{3c^2} uu' \cos \theta \right) \quad (\mu = \text{magnetic permeability} = 1).$$

Crehore⁸ has calculated the forces components according to J. J. Thomson's theory⁹. He finds that the forces are equivalent to

$$F_1 = \frac{ee'}{r^2}, \text{ a repulsion along the line joining the centres.}$$

$$F_2 = \frac{ee'}{c^2 r^2} uu' \cos \theta, \text{ an attraction along the same line.}$$

$$F_3 = \frac{ee'}{r} u', \text{ a force in the direction opposite to the acceleration of the second charge.}$$

$$F_4 = ee' u' \frac{d}{dt} \left(\frac{1}{r} \right), \text{ a force in a direction opposite to the velocity of the second charge.}$$

(3) Sommerfeld¹⁰ has also calculated the ponderomotive forces, assuming that the value of the potential four-vector

$$a = \frac{e[\omega]}{(R\omega)},$$

and using the condition

$$(x-x')^2 + (y-y')^2 + (z-z')^2 + (l-l')^2 = 0$$

in course of differentiation. Their forms are a bit too complicated.

6. Equations of Motion of the Electron.

Minkowski¹¹ deduces the equations of motions of ponderable particle by means of a variational process in which the function

$$\int m_0 c^2 ds, \text{ where } ds^2 = -(dx^2 + dy^2 + dz^2 + dl^2) = c^2 dt^2 \left(1 - \frac{u^2}{c^2} \right)$$

is used instead of the three-dimensional $\int T dt$.

He obtains

$$m_0 c^2 \frac{d^2 x}{ds^2} = X, m_0 c^2 \frac{d^2 y}{ds^2} = Y, m_0 c^2 \frac{d^2 z}{ds^2} = Z, m_0 c^2 \frac{d^2 l}{ds^2} = L. \quad (16)$$

Now we have

$$X = e [w_2 f_{12} + w_3 f_{13} + w_4 f_{14}],$$

according to Lorentz's theorem. We have also

$$\begin{aligned} \frac{d^2 x}{ds^2} &= \left(w_1 \frac{\partial}{\partial x} + w_2 \frac{\partial}{\partial y} + w_3 \frac{\partial}{\partial z} + w_4 \frac{\partial}{\partial l} \right) w_1 \\ &= w_1 \frac{\partial}{\partial x} \left[\frac{1}{2} (w_1^2 + w_2^2 + w_3^2 + w_4^2) \right] + w_2 \left[\left(\frac{\partial w_1}{\partial y} - \frac{\partial w_2}{\partial x} \right) \right. \\ &\quad \left. + w_3 \left(\frac{\partial w_1}{\partial z} - \frac{\partial w_3}{\partial x} \right) + w_4 \left(\frac{\partial w_1}{\partial l} - \frac{\partial w_4}{\partial x} \right) \right] \\ &= -(w_2 \Omega_{12} + w_3 \Omega_{13} + w_4 \Omega_{14}), \text{ putting } \Omega_{hk} = \frac{\partial w_k}{\partial x_h} - \frac{\partial w_h}{\partial x_k}. \end{aligned}$$

Hence we have the four equations, putting $\mu = c^2 m_0 / e$,

$$\left. \begin{aligned} w_2 (f_{12} + \mu \Omega_{12}) + w_3 (f_{13} + \mu \Omega_{13}) + w_4 (f_{14} + \mu \Omega_{14}) &= 0 \\ w_1 (f_{21} + \mu \Omega_{21}) + w_3 (f_{23} + \mu \Omega_{23}) + w_4 (f_{24} + \mu \Omega_{24}) &= 0 \\ w_1 (f_{31} + \mu \Omega_{31}) + w_2 (f_{32} + \mu \Omega_{32}) + w_4 (f_{34} + \mu \Omega_{34}) &= 0 \\ w_1 (f_{41} + \mu \Omega_{41}) + w_2 (f_{42} + \mu \Omega_{42}) + w_3 (f_{43} + \mu \Omega_{43}) &= 0 \end{aligned} \right\}.$$

Of these, only three are independent; the fourth can be deduced from the first three.

We have now identically

$$\begin{vmatrix} f_{12} + \mu \Omega_{12} & f_{13} + \mu \Omega_{13} & f_{14} + \mu \Omega_{14} \\ f_{21} + \mu \Omega_{21} & f_{23} + \mu \Omega_{23} & f_{24} + \mu \Omega_{24} \\ f_{31} + \mu \Omega_{31} & f_{32} + \mu \Omega_{32} & f_{34} + \mu \Omega_{34} \\ f_{41} + \mu \Omega_{41} & f_{42} + \mu \Omega_{42} & f_{43} + \mu \Omega_{43} \end{vmatrix} = 0,$$

$$\text{i.e. } (f_{12} + \mu \Omega_{12})(f_{34} + \mu \Omega_{34}) + (f_{23} + \mu \Omega_{23})(f_{14} + \mu \Omega_{14}) + (f_{31} + \mu \Omega_{31})(f_{24} + \mu \Omega_{24}) = 0. \quad (17)$$

The condition is evidently satisfied if we put

$$-\mu = \frac{f_{12}}{\Omega_{12}} = \frac{f_{23}}{\Omega_{23}} = \frac{f_{31}}{\Omega_{31}} = \frac{f_{14}}{\Omega_{14}} = \frac{f_{24}}{\Omega_{24}} = \frac{f_{34}}{\Omega_{34}}. \quad (18)$$

If of these equations, any three are satisfied the remaining three come out automatically from the equations of motions. But we cannot possibly be sure of the authenticity of these relations unless it can be deduced from an independent source. For this purpose let us take the original variational equations.

Let (X, Y, Z, L) represent the components of the force four-vector at any point, which is subjected to a virtual displacement $\delta x, \delta y, \delta z, \delta l$.

$$\text{Then } \delta W = X\delta x + Y\delta y + Z\delta z + L\delta l,$$

i.e., if we call

$$W = \frac{\partial A}{\partial s}, \quad A = \int W ds,$$

$$\begin{aligned} \delta A &= \int \delta W ds = \int (X\delta x + Y\delta y + Z\delta z + L\delta l) ds \\ &= e \int [f_{12} (dy\delta x - \delta y dz) + f_{23} (dz\delta y - \delta z dy) \\ &\quad + f_{31} (dx\delta z - \delta x dz) + f_{14} (dl\delta x - \delta l dx) + f_{24} (dl\delta y - \delta l dy) \\ &\quad + f_{34} (dl\delta z - \delta l dz)]. \end{aligned}$$

Now the function $\int m_0 c^2 ds$ can also be subjected to a variational process. Since

$$ds = w_1 dx + w_2 dy + w_3 dz + w_4 dl,$$

we find

$$\delta \int m_0 c^2 ds = -m_0 c^2 \int [\Omega_{12} \delta S_{12} + \Omega_{23} \delta S_{23} + \Omega_{31} \delta S_{31} + \Omega_{14} \delta S_{14} + \Omega_{24} \delta S_{24} + \Omega_{34} \delta S_{34}],$$

where

$$\delta S_{hk} = dx_k \delta x_h - \delta x_k dx_h.$$

Thus from the variational equation

$$\delta \int m_0 c^2 ds + \int \delta W ds = 0;$$

i.e., from the principle of least action, keeping the initial and final points fixed, we obtain the original equation

$$\int [(f_{12} + \mu \Omega_{12}) \delta S_{12} + \dots] = 0$$

The relations (18) thus seem to be borne out by independent evidence.

⁸It will be seen that forces F_1, F_2, F_3 are, but for some minor details, represented in our formula. Force F_4 does not occur at all.

⁹Phil Mag., 1913.

¹⁰Ann. d. Phys., Vols. 32 and 33, Über die Relativitäts theorie.

¹¹Minkowski, loc. cit., Anhaup, Mechanics.

Difficulty is encountered here about the interpretation of the terms $(\Omega_{12}, \Omega_{23}, \dots)$ in three dimensions Ω is evidently a six-vector being the four-dimensional curl of the velocity four-vector. The components $[\Omega_{23}, \Omega_{31}, \Omega_{12}]$ are evidently connected with rotations

$$\left[\frac{\delta u_3}{\delta y} - \frac{\delta u_2}{\delta z}, \frac{\delta u_1}{\delta z} - \frac{\delta u_3}{\delta x}, \frac{\delta u_2}{\delta x} - \frac{\delta u_1}{\delta y} \right]$$

and $[\Omega_{14}, \Omega_{24}, \Omega_{34}]$ are connected with the accelerations

$$\left[\frac{d^2x}{dt^2}, \frac{d^2y}{dt^2}, \frac{d^2z}{dt^2} \right]$$

but the exact interpretation in three dimensions has not yet been obtained. We can style Ω as the acceleration six-vector.

On a future occasion, I hope to communicate the result of my investigations on the orbits of the electron under different conditions.

In conclusion, I wish to express my best thanks to my friend, Mr. S. N. Basu, for much help, and useful criticism.

UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA, INDIA.

MAY 11, 1918.

ON THE MECHANICAL AND ELECTRODYNAMICAL PROPERTIES OF THE ELECTRON ADDENDUM

(*Phys. Rev.*, **13**, 238, 1919.)

It appears that the relation

$$-\mu = -\frac{m_0 c^2}{e} = \frac{f_{12}}{\Omega_{12}} = \frac{f_{23}}{\Omega_{23}} = \frac{f_{31}}{\Omega_{31}} = \frac{f_{14}}{\Omega_{14}} = \frac{f_{24}}{\Omega_{24}} = \frac{f_{34}}{\Omega_{34}},$$

which was given in my paper¹ "On the Mechanical and Electrodynamical Properties of the Electron" and which was obtained from the determinant

$$\begin{vmatrix} f_{12} + \mu\Omega_{12} & f_{13} + \mu\Omega_{13} & f_{14} + \mu\Omega_{14} \\ f_{21} + \mu\Omega_{21} & f_{23} + \mu\Omega_{23} & f_{24} + \mu\Omega_{24} \\ f_{31} + \mu\Omega_{31} & f_{32} + \mu\Omega_{32} & f_{34} + \mu\Omega_{34} \\ f_{41} + \mu\Omega_{41} & f_{42} + \mu\Omega_{42} & f_{43} + \mu\Omega_{43} \end{vmatrix} = 0$$

or

$$(f_{12} + \mu\Omega_{12})(f_{34} + \mu\Omega_{34}) + (f_{23} + \mu\Omega_{23})(f_{14} + \mu\Omega_{14}) + (f_{31} + \mu\Omega_{31})(f_{24} + \mu\Omega_{24}) = 0,$$

cannot hold. For, from the principle of least action written in Minkowski's form,

$$\delta \int m_0 c^2 ds - \int \delta W \cdot ds = 0,$$

we obtain the relation

$$\iint [(f_{12} + \mu\Omega_{12})(dx\delta y - \delta x dy)] + 5 \text{ other similar terms} = 0.$$

But it is not possible to equate to zero the coefficients of the six-components $(dx\delta y - \delta x dy)$ of the area-six-vector $(dSx\delta s)$ as done in that paper, for though $(\delta x, \delta y, \delta z, \delta l)$ represent an arbitrary displacement (dx, dy, dz, dl) , is not so, but represent the actual displacements. We have, therefore, to collect the coefficients of $(\delta x, \delta y, \delta z, \delta l)$ and put them separately equal to zero. In this way we obtain

$$\begin{aligned} -\frac{m_0 c^2}{e} &= \frac{f_{12}w_2 + f_{13}w_3 + f_{14}w_4}{\Omega_{12}w_2 + \Omega_{13}w_3 + \Omega_{14}w_4} = \frac{f_{21}w_1 + f_{23}w_3 + f_{24}w_4}{\Omega_{21}w_1 + \Omega_{23}w_3 + \Omega_{24}w_4} \\ &= \frac{f_{31}w_1 + f_{32}w_2 + f_{34}w_4}{\Omega_{31}w_1 + \Omega_{32}w_2 + \Omega_{34}w_4} = \frac{f_{41}w_1 + f_{42}w_2 + f_{43}w_3}{\Omega_{41}w_1 + \Omega_{42}w_2 + \Omega_{43}w_3} \quad (A) \end{aligned}$$

which are simply another form of the Minkowskian equations

$$m_0 c^2 \frac{d^2x}{ds^2} = X, \quad m_0 c^2 \frac{d^2y}{ds^2} = Y, \quad m_0 c^2 \frac{d^2z}{ds^2} = Z, \quad m_0 c^2 \frac{d^2l}{ds^2} = L \quad (A')$$

$$\text{for} \quad \frac{d^2x}{ds^2} = -(w_2\Omega_{12} + w_3\Omega_{13} + w_4\Omega_{14}), \text{ etc.}$$

The form (A) as it involves the acceleration six-vector may for certain purposes prove more convenient than the form (A').

¹*Physical Review*, January, 1919.

8. ON RADIATION-PRESSURE AND THE QUANTUM THEORY

A PRELIMINARY NOTE

(*Astrophys. Journ.*, **50**, 220, 1919.)

After the prediction by Maxwell of the existence of the pressure of radiant energy on the basis of his theory of stresses and strains in ether, other ways of arriving at the same result have been found by Bartoli (thermodynamical), Poynting (flow of momentum along a ray of light), and Larmor (electromagnetic wave-theory of light). A review of these methods shows that they are all statistical, i.e., the result holds only when the surface encountered by radiation is large compared with the wave of light and is thickly set with matter.

Schwarzschild and more recently Nicholson¹ and Klotz² have worked out, on the basis of the continuous theory, the value of the radiation-pressure, when the size of the obstructing mass is gradually decreased, ultimately being reduced to the scale of the wave-length of light. In this case the effect of repulsing light-pressure gradually preponderates over any gravitative force to which the particle may be subject, but at the same time it appears that there is a limit to this process of reduction. If the particle be too small, it is no longer capable of acting as a barrier to the advancing light-waves, and consequently experiences no radiation-pressure. It appears from these investigations that for particles of the molecular size (radius= 10^{-8} cm) the effect of light-pressure is totally evanescent.

But this conclusion from the old continuous theory is rather contradictory to the requirements of astrophysics, for in order to explain tails of comets and other astrophysical phenomena (such as solar prominences, corona) which take place on the surface of luminous heavenly bodies we have to assume the existence of certain repulsive forces³ (levity) acting on the ultimate gaseous molecules and thus reducing the gravitational attraction on them. But a still stronger ground for rejecting the conclusion is furnished by the experimental demonstration by Lebedew⁴ of the existence of radiation-pressure on molecules of absorbing gases like CO₂, methane, propane, etc. It may thus be taken for granted, in spite of the failure of the continuous theory, that the molecules do really suffer a radiation-pressure, which in the aggregate conforms to Maxwell's law.

Professor R. W. Wood⁵ is inclined to the opinion that the

gas molecule may be capable of stopping the radiation by resonance, and may thus experience a radiation-pressure, but precisely what is meant by stoppage of radiation by resonance is not clear. An explanation of the existence of radiation-pressure on molecules is furnished when we apply the quantum theory in the place of the old continuous theory of light. Instead of assuming that "light" is spread continuously over all points of space, let us suppose that they are localized in pulses of energy $h\nu$ (ν =frequency of light, h =Planck's universal radiation constant). Let this pulse encounter a molecule m and be absorbed by it. Then in doing so the molecule will be thrust forward with an impulsive momentum of $\frac{h\nu}{c}$ (c =velocity of light); for we may suppose the pulse to have the mass $\frac{h\nu}{c^2}$ and the momentum $\frac{h\nu}{c}$; the absorption of the pulse by the molecule may be taken as a case of inelastic impact, the whole momentum being communicated to the molecule. The velocity with which the molecule will move forward= $\frac{h\nu}{cm}$.

Let us consider the effect of the absorption of a pulse of the hydrogen light corresponding to the line H α by the hydrogen atom. The velocity imparted at each kick of light

$$v = \frac{h\nu}{cm} = 60 \text{ cm per second,}$$

$$(\text{taking } h = 6.54 \times 10^{-21})$$

$$\frac{c}{\nu} = \lambda = 6.563 \times 10^{-5} \text{ cm.; } m = \frac{1}{6.062 \times 10^{23}} \text{ gms.}$$

This velocity is rather a small quantity (compared to the orbital velocity of the molecules), but it should be remembered that it is really an impulsive velocity and is of the nature of an acceleration. The total velocity acquired by a hydrogen atom per second will depend upon the number of kicks of light it experiences per second, and provided this is sufficiently great the velocity acquired may rise to enormous values. But a priori we cannot say what this number will amount to without a preliminary examination of the physical conditions.

This conclusion explains Lebedew's results, which cannot be explained by the continuous theory, and at the same

¹*Monthly Notices*, **74**, 425, 1914.

²*Journal of the R.A.S. of Canada*, **12**, 357, 1918.

³See Agnes M. Clerke, *Problems of Astrophysics*, p. 51.

⁴*Annalen Physik*, **92**, 411, 1910.

⁵*Physical Optics*, p 51.

time offers a general explanation of the radiation-pressure.

The pressure $= \frac{1}{c} \sum \Sigma h\nu$, where the summation extends over all the pulses absorbed in unit time, within unit area. It thus equals AI , where I = intensity of light, A = fraction absorbed. The aggregate effect remains unchanged, but it is now supposed to be concentrated on a few active molecules, the inactive molecules remaining unaffected.

The explanation offered closely resembles Einstein's explanation of the velocity of emission of the photo-electrons. According to Einstein when a pulse of light ($h\nu$) falls upon an atom it is instantly absorbed and goes to increase the energy of the system. Consequently certain of the electrons of an atomic system acquire a velocity which is greater than the critical velocity required for retaining these electrons in their orbit. Let A be the energy required for detaching an electron from the parent atom. Then the velocity of escape is given by the law

$$\Sigma \frac{1}{2}mv^2 = h\nu - \Sigma A.$$

The maximum velocity occurs when only one electron is emitted. Then

$$\frac{1}{2}mv^2 = h\nu - A.$$

Actual experiments by Millikan⁶ and others have established the truth of the law quantitatively. Besides, the phenomenon is instantaneous whatever be the intensity of the light. This feature is not capable of explanation by the continuous theory of absorption. N. R. Campbell⁷ has found that in certain cases the continuous theory requires that the atom must be illuminated for at least 15 minutes before it can acquire the energy sufficient for the emission of the electron, while actually the emission takes place in less than $\frac{1}{100000}$ of a second after illumination.

Let us now see how the number of kicks of light experienced by the hydrogen atom or molecule varies with the existing circumstances. The number will clearly depend upon the following factors: (1) the density of pulses of light in the region traversed by the molecule; (2) the time of retention by the molecule or the atom of the capacity for the absorption of light. We shall first take the second point. Hydrogen under ordinary circumstances does not absorb its characteristic radiation (represented by the Balmer lines), as has been demonstrated by the repeated failures of the experiments for obtaining the reversal of the hydrogen lines. But the experiments of Ladenburg and Loria⁸ have thrown a new light on the cause of these failures; they find that hydrogen is capable of absorbing its characteristic radiation only when it is in an active state, i.e., when it is in a state of luminescence. This conclusion is also borne out by the theoretical investigations of Bohr⁹,

for according to his theory a hydrogen line is emitted when the attendant electron leaps from orbit 3 to orbit 2, while in the natural state the electron is at orbit 1. We may symbolically express the idea as in Fig. 1.

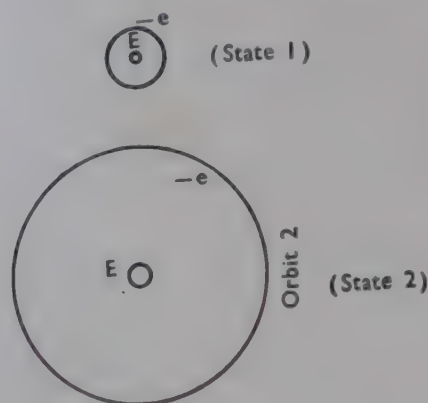


FIG. 1

State 1, natural state when inactive for the Balmer lines.

State 2, active state (when emitting the Balmer lines).

In order that an H atom may absorb a Balmer line, it must be, to start with, at state 2.

We may thus take it for granted that the H atoms which absorb the Balmer lines are not the ordinary H atoms, but an active modification thereof,

the electron being at orbit 2 instead of at orbit 1. When light corresponding to any line of the Balmer spectrum traverses a mass of hydrogen, it is only the active particles which will absorb this light and be subjected to the impulsive kicks of this light.

Taking it for granted that an active molecule suffers a discontinuous kick of light given by the formula in the process of absorption, let us see how it will behave when placed in a field of radiation. To visualize matters, we shall take an active H atom moving near the photosphere of the sun. The H atom, if active to start with, will pick out from the continuous spectrum the pulse corresponding to $H\alpha$ or $H\beta$ and with an instantaneous velocity of 60 to 31 cm per second. It is true that, as the particle emits light, it suffers an equal recoil opposite to the direction of emission. It should be borne in mind that the emission does not take place in any specified direction, but in any direction according to the law of chance, while the pulses which are absorbed come from a specified direction, viz., the center of the sun. Hence if the particle continues active for a sufficient length of time, the H atom may ultimately acquire a velocity exceeding the critical velocity of 6.12×10^7 cm per sec. (the velocity required for the escape of the particle from the gravitational influence of the sun).

The precise velocity which a particle acquires depends upon a large number of unknown factors: (1) the intensity of the field of radiation—the influence of this factor is to a certain extent known—the density of pulses varies as the intensity of light, and therefore follows the law of inverse square; (2) the persistence of the activity of the H atom, or rather, if the activity be lost, the quickness with which it is regenerated; (3) the actual proportion of active particles in any region.

Nothing is known about the second and the third factors; consequently it is not possible to work out a quantitative

⁶ *Physical Review*, 7, 18, 1916.

⁷ *Modern Electrical Theory*, p. 249.

⁸ *Verhandlungen der deutschen Physikalischen Gesellschaft*, 10, 858, 1908.

⁹ *Philosophical Magazine*, 26, 1, 476, 857, 1913.

theory of the effect of radiation-pressure on the expulsion of the molecules. But the general considerations show that radiation-pressure may exert an effect on the atoms and molecules which are out of all proportion to their actual sizes. It also shows that the radiation-pressure exerts a sort of sifting action on the molecules, driving the active ones radially outward along the direction of the beam. The cumulative effect of the pulses may be sufficiently great to endow the atoms with a large velocity—the velocity with which the tops of solar prominences are observed to shoot up.

The velocity of the red prominences are sometimes found to be as high as 6×10^7 cm per second.

The solar prominences have sometimes been explained on the assumption that they are due to the convection of hot masses of vapor from the solar photosphere, which, after reaching the atmosphere, are supposed to expand adiabatically and develop the large velocities with which the prominences are observed to shoot up. But both Pringsheim and Nicholson¹⁰ have pointed out several insuperable difficulties in the way of the acceptance of this hypothesis, including the deduction that the maximum velocity obtainable from adiabatic expansion is less than $\frac{1}{45}$ of the velocity with which the prominences are observed to shoot forward (6×10^7 cm). Nicholson has suggested that some unknown forces of electrical origin may be the cause of these large velocities, but even granting that the electrical fields exist in the sun it is difficult to see how this can act upon the luminous hydrogen particles, which are most probably uncharged. According to the hypothesis put forward in this paper, the effect of radiation-pressure on the separate particles is altogether disproportionate to the dimensions of the particles and may cause them to be

endowed with a "levity"¹¹ long sought for in the explanation of the prominences, the corona, and other solar phenomena, including the extension of the solar atmosphere.¹² The hypothesis presents the problem of the radiative equilibrium of the solar atmosphere in a new light.

These ideas may be applied to the explanation of the tails of comets. The tails of comets are undoubtedly caused by some sort of repulsive action exerted by solar light, but since, on the older theory, the effect was found evanescent on particles of the molecular size, the tail was supposed to consist of some sort of cosmic dust. But the spectroscopic examination of the light from the tails shows that they consist, at least partly, of luminous gases (CO , CO_2)¹³. Now the explanation is quite easy, if the considerations advanced in this paper hold. As the comet approaches the sun, more and more pulses of light from the sun traverse the nucleus and the coma. Light-pulses of suitable frequency are picked up by the gaseous particles, which thus gradually gain in velocity in a direction away from the sun. The cumulative effect of the absorbed pulses may endow the particle with a velocity sufficient for its escape from the main mass of the cometary matter and form into the tail.

It is hoped to develop these ideas further in a future communication.

UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.

MARCH 4, 1919.

¹¹ Ch. Fabry, lecture delivered before the Astronomical Society of France, 1918 (*L'Astronomie*, **32**, 14, 1918).

¹² Attention may be called to a comprehensive paper by D. Brunt (*Monthly Notices*, **73**, 568, 1913), who has shown that neither of the three theories of the equilibrium of the solar atmosphere (isothermal, adiabatic, or radiative) can account for an atmosphere extending to the observed height of the solar atmosphere. The results of the spectroheliographic observations are distinctly unfavorable to Julius' theory of anomalous dispersion (see *Astrophysical Journal*, Papers by Hale, St. John, and others).

¹³ Bohr, *loc cit.*

¹⁰ *Monthly Notices*, **74**, 425, 1914.

9. ON THE FUNDAMENTAL LAW OF ELECTRICAL ACTION¹

(*Phil. Mag.*, *Sr. VI*, **37**, 347, 1919)

1.

In the present paper an attempt has been made to determine the law of attraction between two moving electrons, with the aid of the New Electrodynamics as modified by the Principle of Relativity. The problem is a rather old one, and seems to have first occurred in 1835 to Gauss², from whom the title of the paper has been borrowed. Before explaining my methods, I shall give a short history of the problem.

About the year 1826 Ampère published his celebrated laws of electrodynamic action, which enable us to calculate, with strict mathematical exactness, the action between two closed electric currents. If we assume that a current of electricity consists of streams of positive and negative charges moving in opposite directions, this action between two closed currents is seen to be composed of the elementary actions between the moving charges, taken two and two. The moving charges, therefore, cannot attract or repel in the same manner as two stationary charges (*viz.* force $= ee'/r^2$), for in that case the total action would be zero.

¹ Communicated by Prof. D. N. Mallik.

² Much of the Introduction is taken from Maxwells' 'Electricity and Magnetism', Chaps. II and XXIII, see especially pp. 483 *et seq.*

The natural assumption is that the law of attraction in this case is quite different, and it depends not only upon mutual distance between the two electrons, but also upon their velocities. This is the problem which Gauss set himself to answer; he does not of course speak of electrons, but of charged particles, which mathematically amounts to the same thing.

Gauss and his followers adopted a deductive method for solving this problem. Ampère had given the law which should subsist between two elements of current, i.e. the currents flowing through an element of length of a circuit in order to account for the action between two closed currents. This law was derived partly from the Geometry of lines, partly from experiments, and besides, involved a number of assumptions. The solution was therefore not quite convincing, and, indeed, as Grassmann³ and Stefan⁴ subsequently proved, was not a unique one. Three other expressions were found to be as good as Ampère's expression for the action between two elements of current. Still, Ampère's solution seemed to be most likely, because the assumptions were simpler in this than in other cases.

Starting with Ampère's expression for the action between two elements of current, and introducing the further assumption that the current consists of discrete charged particles in motion, Gauss deduced the following expression for the mutual attraction between two charges:

$$F = \frac{ee'}{r^2} \left[1 + \frac{1}{c^2} \left(u^2 - \frac{3}{2} \left(\frac{du}{dt} \right)^2 \right) \right],$$

where e, e' are the charges, r =mutual distance, u =relative velocity.

But the law was found to be inconsistent with the principle of conservation of energy, and naturally fell through.

Other physicists in turn took up the problem. The most celebrated formula is that of Weber⁵, according to whom the mutual potential of two moving charges is given by the expression

$$\psi = \frac{ee'}{r} \left[1 - \frac{1}{2c^2} \left(\frac{\partial r}{\partial t} \right)^2 \right].$$

This formula is consistent with the principle of conservation of energy, but was nevertheless found by Helmholtz⁶ to lead to improbable results.

These laws were all based on the idea of action at a distance. But in 1845, Gauss⁷ again returned to the problem (which he now calls the real keystone of electrodynamics), with the idea that the action, instead of being propagated instantaneously, may be propagated with a finite velocity in a manner similar to that of light. But he did not succeed,

as he himself tells us, in forming any consistent mental picture of the manner in which the action is propagated, and seems to have given up the attempt.

Three other mathematicians, Riemann, Neumann and Betti⁸ followed in the wake of Gauss, and suggested solutions, but these also have been no more successful than their predecessors. According to Riemann⁹, the force components between two charges are given by the Lagrangian derivatives of the function

$$\psi = \frac{ee'}{R} \left[1 - \frac{(u-u')^2 + (v-v')^2 + (w-w')^2}{c^2} \right],$$

where (u, v, w) are the velocities of the one particle, (u', v', w') are the velocities of the other.

According to all of these theories, the action depends on the relative velocity of the two particles. This can be at once perceived by a reference to the formulae of Gauss, Weber and Riemann. If both particles move with the same velocity, the action would be the same as that between two stationary ones, and there would not be any electrodynamical action. This is a very objectionable feature of these theories, and attention to this fact was first drawn, I believe, by Clausius.¹⁰ Clausius is also the author of a series of elaborate investigations on this point. According to his theory, the components of the force between two electrified particles are the Lagrangian derivatives of the function

$$\phi = \frac{ee'}{R} \left[1 - \frac{uu' \cos \theta}{c^2} \right],$$

u and u' being the velocities of the two particles, θ being the angle between their directions of motion. The force components are given by the expressions

$$X = \frac{\partial \phi}{\partial x} - \frac{d}{dt} \left(\frac{\partial \phi}{\partial \frac{dx}{dt}} \right), \quad Y = \frac{\partial \phi}{\partial y} - \frac{d}{dt} \left(\frac{\partial \phi}{\partial \frac{dy}{dt}} \right),$$

$$Z = \frac{\partial \phi}{\partial z} - \frac{d}{dt} \left(\frac{\partial \phi}{\partial \frac{dz}{dt}} \right).$$

It will be observed that the action depends not upon the relative velocity, but upon the absolute velocities of the two particles. Clausius indeed proceeds to show that his formula, besides leading to Ampère's laws of Electrodynamical action, is remarkably free from the objections which were raised against the other formulae.

Clausius's formula may be said, in a way, to have been confirmed by the investigations of J. J. Thomson.¹¹ Thomson investigated, from Maxwell's theory of moving tubes of force, the action between two spheres of radii a and a' ,

³ Loc. cit. p. 174.

⁴ *Populäre Schriften-Boltzmann*, pp. 95 & 96.

⁵ Maxwell, loc. cit. pp. 484 & 485.

⁶ *Phil. Mag.*, December 1872.

⁷ Maxwell, loc. cit. p. 490.

⁸ Maxwell, loc. cit. p. 490.

⁹ Clausius, *Phil. Mag.*, 1880.

¹⁰ *Journal für Mathematic* (Crelle's Journal), Vols. lxxxii & lxxxiii; *Phil. Mag.*, 1880.

¹¹ *Phil. Mag.*, 1881. 'Application of Dynamics to Problems of Physics and Chemistry', Chap IV.

moving with the velocities u and u' and carrying the charges e and e' . The kinetic energy was found to be

$$\left(\frac{1}{2}m + \frac{1}{18}\frac{\mu e^2}{a}\right)u^2 + \left(\frac{1}{2}m' + \frac{1}{18}\frac{\mu e'^2}{a'}\right)u'^2 + \frac{\mu e e' \cos \theta u u'}{3R}$$

Neglecting the terms due to the Mass-motion, the Lagrangian Function $T-U$, for the two charged particles, is easily seen to be equivalent to

$$\frac{\mu}{3} \left(\frac{u u' \cos \theta}{R} \right) - \frac{1}{kR}.$$

The similarity of this form with the Clausius form is apparent. There is of course discrepancy in the $\left(\frac{\mu}{3}\right)$ term.

These formulae are all limited to the case where the velocities of the moving charges are small compared with the velocity of light.

From what has been said before, it will be seen that the problem is still an open one. The investigations hitherto given are largely empirical, and not based on sufficient theoretical basis. In view of the recent extraordinary development of electronic physics, it cannot be said that the importance of the problem has been in any way diminished. On the contrary, a knowledge of the laws of electronic attraction and a clear formulation of the dynamics of the electron are necessary before we can satisfactorily handle any problem on electronic physics,—such as the atomic model, or radiation from atoms and electrons.

2.

In the present investigation I have throughout used the New Electrodynamics (i.e., as modified by Lorentz, Einstein, and Minkowski according to the Principle of Relativity). I have particularly used the method of four-dimensional analysis which was first initiated by Minkowski.¹² A large amount of work in this line has been done by Born¹³ and Sommerfeld,¹⁴ though not always with the same specific purpose which I have in this paper. Sommerfeld in particular, in connexion with his development of four-dimensional analysis, has investigated the law of attraction between two moving electrons; but the result obtained is so cumbrous as to make further progress almost impossible. This is due to the fact that for the scalar and vector potential of the field produced by a moving electron, they arrived at an expression which is only a partial statement of the complete result (see remarks at the end of § 8). When this complete result is introduced, the electric and magnetic forces as well as the ponderomotive force acting on an electron come out in very elegant forms, enabling us ultimately to write out the equations of motion of two electrons round each other in a Lagrangian form. When

one electron is at rest, the equations lead to Darwin's results (*Phil. Mag.*, 1915).

3. Notation

The notation used in this paper is identical with that used by Minkowski and Sommerfeld in the memoirs just mentioned, and is to be found in any one of general treatises on Relativity (Cunningham or Silberstein). However, for the convenience of the reader, it is explained below.

The unit of time used in this paper is $\frac{1}{c}$ times the ordinary unit (c , velocity of light measured in ordinary C. G. S. units), so that with this notation, the velocity of light becomes unity.

We shall, in most cases, use $l = \sqrt{-1} t$ so that (x, y, z, l) denotes the space-time coordinates of world-point (Welt-punkt). The quantities

$$(\omega_1, \omega_2, \omega_3, \omega_4) = \frac{1}{\sqrt{1-u^2}}(u_1, u_2, u_3, \sqrt{-1}),$$

where (u_1, u_2, u_3) are the ordinary space components of the velocity of a material point, will denote the space-time components of the Velocity-four-vector. It should be noticed that $(u_1, u_2, u_3) = \frac{d}{dt}(x, y, z)$, and if by τ we denote the proper-time (Eigenzeit) of motion of the material point, we shall have $d\tau = dt\sqrt{1-u^2}$, and

$$(\omega_1, \omega_2, \omega_3, \omega_4) = \frac{d}{d\tau}(x, y, z, l).$$

$\mathbf{a}$ will denote a four-vector of which the space components are equivalent to the vector-potentials used in Electrodynamics, the time-component $= \sqrt{-1} \phi$, where ϕ is the ordinary scalar-potential. This is known as the Potential-four-vector.

The operator

$$\left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z} + l\frac{\partial}{\partial l}\right),$$

which plays the same role in the four-dimensional analysis as the familiar operator ∇ in three-dimensions

$$\left(\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right),$$

was called by Minkowski "Lor", in honour of H. A. Lorentz, the discoverer of the Principle of Relativity.

It is denoted by $\square$.

The operator

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial l^2}\right),$$

which corresponds to the three-dimensional operator

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right),$$

is generally denoted by $\square^2$.

The set of four quantities $\rho(u_1, u_2, u_3, i)$, where ρ = density of electricity at a point, is a four-vector according to Lorentz and Einstein. It is known as the Stream-four-vector and will be denoted by S .

¹² H. Minkowski, *Mathematische Annalen*, vol. lxxviii. p. 472 et seq.

¹³ Born, *Ann. d. Physik*, vol. xxviii, p. 571.

¹⁴ Sommerfeld, *Ann. d. Physik*, vol. xxxiii. pp. 649 et seq; vol. xxxii pp. 749 et seq.

4.

The potential-four-vector $\mathbf{a}$ satisfies the equations¹⁵
 $\square^2 \mathbf{a} = -4\pi S$, or $\square^2 \mathbf{a} = 0$, ... (1)

according as the world-point at which $\square^2 \mathbf{a}$ is taken is occupied by a stream-four-vector or is empty.

$\mathbf{a}$ satisfies also the equation

$$\text{Div } \mathbf{a}, \text{ or } (\square \mathbf{a}) = 0 \quad \dots (2)$$

at all points of the world-space.

Now the fundamental solution of equations (1), due to a single stream-four-vector S , occupying the world-point (x', y', z', l') is

$$\frac{AS}{r^2}, \text{ or } A \frac{S}{(x-x')^2 + (y-y')^2 + (z-z')^2 + (l-l')^2}, \quad \dots (3)$$

where (x, y, z, l) is the world-point at which $\mathbf{a}$ is to be estimated.

A can be proved to be equivalent to $\frac{1}{\pi}$.

Therefore the potential-four-vector at a world-point (x, y, z, l) due to a distribution in the world-space of the stream-four-vector S is

$$\mathbf{a} = \frac{1}{\pi} \iiint \frac{S dx' dy' dz' dl'}{(x-x')^2 + (y-y')^2 + (z-z')^2 + (l-l')^2}, \quad (3')$$

N.B. In modern methods of treating problems of Electrodynamics, the usual practice is to choose a unit of current which is $\sqrt{4\pi}$ times smaller than the ordinary unit, thereby instead of having $\square^2 \mathbf{a} = -4\pi S$, we have $\square^2 \mathbf{a} = -S$. I have struck to the older method, because this is more convenient for our purpose.

The fundamental solution $\frac{1}{r^2}$ seems to have been first

obtained by Poincaré.¹⁶ It corresponds to the solution $\frac{1}{r}$ in three-dimensional problems on Potential, and is a particular case of the following general result first obtained by Poincaré.¹⁷

If $(x_1, x_2, \dots, x_n)$ be the coordinates of a point in space of n -dimensions, the fundamental solution of the generalized Laplacian

$$\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \dots + \frac{\partial^2}{\partial x_n^2} \right) V = 0,$$

is $\frac{A}{r^{n-2}}$, where $r^2 = (x_1 - x_1')^2 + (x_2 - x_2')^2 + \dots + (x_n - x_n')^2$... (4)

5. *Potential-four-vector at an external point due to the motion of a point-charge.*

By a point-charge is meant a charge having no extension in ordinary space. In four-dimensions, however, it has extension in one direction, viz, in the direction of the time-axis if the electron be stationary, or along an axis making

an angle of $(\tan^{-1}u)$ with the time-axis, if u be its velocity of motion.

Let (x, y, z, l) be the coordinates of the point-charge, which we suppose to have started from the origin at time $t=0$. Then we have $(x, y, z) = -\sqrt{-1} (u_1, u_2, u_3)$. Let (a, b, c, λ) be the coordinates of the external point at which the potential $\mathbf{a}$ is sought. According to the general theorem in the previous section, the potential-four-vector $\mathbf{a}$ is given by the integral

$$\int_{-\infty}^{\infty} \frac{\rho_o(\omega) dl'}{(x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2},$$

where $\rho_o(\omega) = \rho(u_1, u_2, u_3, \sqrt{-1})$, and therefore $\rho_o = \rho \sqrt{1-u^2}$, the rest-density, which is an invariant according to Lorentz and Einstein,

dl' = an element of length along the axis of motion; dl' is easily seen to be equivalent to $dl \sqrt{1-u^2}$.

$$\begin{aligned} \text{Now } (x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2 \\ = l^2 (1-u^2) + 2il (u_1 a + u_2 b + u_3 c + i\lambda) + a^2 + b^2 + c^2 + \lambda^2 \\ = l'^2 + 2il' (\omega_1 a + \omega_2 b + \omega_3 c + \omega_4 \lambda) + a^2 + b^2 + c^2 + \lambda^2. \end{aligned}$$

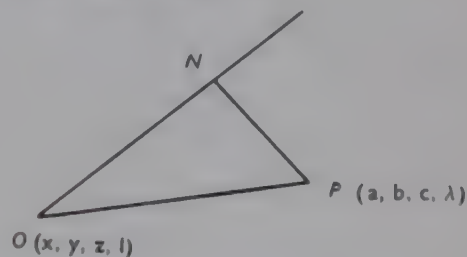
Putting $l' = l \sqrt{1-u^2}$,

this integral is easily seen to be equivalent to

$$\frac{\rho_o(\omega)}{[a^2 + b^2 + c^2 + \lambda^2 + (a\omega_1 + b\omega_2 + c\omega_3 + \lambda\omega_4)^2]^{\frac{1}{2}}} \quad \dots (5)$$

With the aid of four-dimensional geometry, we can give an interesting interpretation to this expression. The direction of motion of the charge (ρ) is given by the line

$$\frac{x}{\omega_1} = \frac{y}{\omega_2} = \frac{z}{\omega_3} = \frac{l}{\omega_4}.$$



Let P be the point (a, b, c, λ) . Then we have

$$PN^2 = OP^2 - ON^2$$

$$= (a^2 + b^2 + c^2 + \lambda^2) + (a\omega_1 + b\omega_2 + c\omega_3 + \lambda\omega_4)^2,$$

for ON = projection of OP on $OA = i(\omega_1 a + \omega_2 b + \omega_3 c + \omega_4 \lambda)$.

Thus the denominator in the expression (5) is seen to be equivalent to R , where R is the perpendicular distance from the external point on the axis of motion.

The result can also be easily proved if we introduce a Lorentz-transformation, by which the axis of motion becomes the new-time-axis. Then in the expression (4), the four-vector $\rho_o(\omega)$ becomes

$$\rho_o(0, 0, 0, \sqrt{-1}),$$

and the problem is reduced to one at rest. The denominator becomes equivalent to $R^2 + l'^2$ where R is the perpendicular from P on the axis of motion.

¹⁵ Born, *Ann. d. Physik*, vol xxviii. p. 571.

¹⁶ Sommerfeld, *Ann. D. Physik*, vol. xxxiii. p. 663.

¹⁷ *Théorie du Potential Newtonien*.

We have therefore

$$\mathbf{a}' = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\rho_o(i) dl'}{R^2 + l'^2} = \frac{\rho_o(0,0,0,i)}{R},$$

Now $(0, 0, 0, \mathbf{a}_4)$ are the components, in the transformed system, of potential-four-vector $\mathbf{a}'$ whose components in the original system are $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4)$. Re-transforming to the original system, we have

$$[\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4] = \frac{\rho_o(\omega_1, \omega_2, \omega_3, \omega_4)}{R} \dots (6)$$

Otherwise—When by means of an orthogonal Lorentz-transformation, we transform from the system (x, y, z, l) to the system (x', y', z', l') , the generalised Laplacian $\square^2 \mathbf{a}$ is transformed to

$$\left(\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2} + \frac{\partial^2}{\partial l'^2} \right) \mathbf{a} = 0, \text{ or } -4\pi S'.$$

In the present case, the distribution on an infinite line is along the l' axis. Therefore $\mathbf{a}$ must be independent of l' from which

$$\mathbf{a} = \frac{S'}{\sqrt{x'^2 + y'^2 + z'^2}}.$$

$\sqrt{x'^2 + y'^2 + z'^2}$ is easily seen to be equivalent to what we have called R previously.

Thus according to this method of investigation also, the potential-four-vector

$$\mathbf{a} = \frac{\rho_o(\omega_1, \omega_2, \omega_3, \omega_4)}{R}, \dots (6)$$

where R =perpendicular distance from the external point (a, b, c, λ) on the axis of motion of the point-charge:—direction cosines $\sqrt{-1}(\omega_1, \omega_2, \omega_3, \omega_4)$.

6. The Ponderomotive Force¹⁵.

If $\mathbf{a}$ be the potential-four-vector in an electric field, and ρ be the electric space-density at a point, the force acting on this point is given by the matrix

$$\rho \begin{vmatrix} u_1 & u_2 & u_3 & i \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} & \frac{\partial}{\partial l} \\ \mathbf{a}_1 & \mathbf{a}_2 & \mathbf{a}_3 & \mathbf{a}_4 \end{vmatrix} \dots (7)$$

It should be noticed that the word "Force" is used in a generalised sense. The components of this four-vector are (X, Y, Z) the ordinary space-components, and

$$L = i(Xu_1 + Yu_2 + Zu_3),$$

i.e., $\sqrt{-1}$ times the rate of doing work. The four components are connected by the equation

$$X\omega_1 + Y\omega_2 + Z\omega_3 + L\omega_4 = 0,$$

i.e., the force-four-vector is always normal to the velocity-four-vector.

Writing (ϕ, F, G, H) for $(\sqrt{-1} \mathbf{a}_4, \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ and

introducing the ordinary C.G.S. units, it can be easily verified that this expression is identical with Lorentz's expression for Ponderomotive force.

We shall now write $(\omega_1, \omega_2, \omega_3, \omega_4)$ instead of $(u_1, u_2, u_3, \sqrt{-1})$. Then

$$[X, Y, Z, L] = \rho_o \begin{vmatrix} \omega_1 & \omega_2 & \omega_3 & \omega_4 \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} & \frac{\partial}{\partial l} \\ \mathbf{a}_1 & \mathbf{a}_2 & \mathbf{a}_3 & \mathbf{a}_4 \end{vmatrix}.$$

$\rho_o = \rho \sqrt{1-u^2}$ is an invariant, and is generally known as the rest-density,

and $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4) = \frac{\rho_o' \omega'}{R'}.$

R' =perpendicular distance from the external point (x, y, z, l) on the axis of motion of the charge ρ' which produces the field.

The coordinates here refer to the coordinates of the point-charges.¹⁹

7. Law of Attraction between two Point-charges.

We have now

$$X = \rho_o \left[\left\{ \omega_1 \frac{\partial \mathbf{a}_1}{\partial x} + \omega_2 \frac{\partial \mathbf{a}_2}{\partial x} + \omega_3 \frac{\partial \mathbf{a}_3}{\partial x} + \omega_4 \frac{\partial \mathbf{a}_4}{\partial x} \right\} - \left\{ \omega_1 \frac{\partial}{\partial x} + \omega_2 \frac{\partial}{\partial y} + \omega_3 \frac{\partial}{\partial z} + \omega_4 \frac{\partial}{\partial l} \right\} \mathbf{a}_1 \right],$$

i.e.,

$$X = \rho_o \rho_o' \left[(\omega_1 \omega_1' + \omega_2 \omega_2' + \omega_3 \omega_3' + \omega_4 \omega_4') \frac{\partial}{\partial x} \left(\frac{1}{R'} \right) - \left(\omega_1 \frac{\partial}{\partial x} + \omega_2 \frac{\partial}{\partial y} + \omega_3 \frac{\partial}{\partial z} + \omega_4 \frac{\partial}{\partial l} \right) \left(\frac{\omega_1'}{R'} \right) \right]$$

for in the expression for $\mathbf{a}$, R is the only term explicitly involving the coordinates (x, y, z, l) , (ρ_o', ω') being independent of them.

Now let $d\tau$ =proper time (Eigenzeit) of motion of A. Then $d\tau = dt \sqrt{1-u^2}$,

$$\text{and } (\omega_1, \omega_2, \omega_3, \omega_4) = \frac{d}{d\tau}(x, y, z, l).$$

We have therefore

$$\begin{aligned} \frac{d}{d\tau} &= \frac{\partial}{\partial x} \cdot \frac{dx}{d\tau} + \frac{\partial}{\partial y} \cdot \frac{dy}{d\tau} + \frac{\partial}{\partial z} \cdot \frac{dz}{d\tau} + \frac{\partial}{\partial l} \cdot \frac{dl}{d\tau} \\ &= \omega_1 \frac{\partial}{\partial x} + \omega_2 \frac{\partial}{\partial y} + \omega_3 \frac{\partial}{\partial z} + \omega_4 \frac{\partial}{\partial l} \end{aligned}$$

If we now put

$$\phi = \frac{\omega_1 \omega_1' + \omega_2 \omega_2' + \omega_3 \omega_3' + \omega_4 \omega_4'}{R'} \rho_o \rho_o', \dots (8)$$

then, since

$$(\rho_o \rho_o' \omega_1' / R') = \frac{\partial \Phi}{\partial \omega_1},$$

¹⁹ The matrix used for expressing the Ponderomotive Force (X, Y, Z, L) has not been used in the conventional sense (Sommerfeld, *Ann. der Physik*, Vol. xxxii & xxxiii) as can be easily observed.

we have

$$X = \frac{\partial \Phi}{\partial x} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_1} \right).$$

Similarly for the other components (Y, Z, L).

The form is Lagrangian, and the expression for (X, Y, Z, L) comes out in the form originally pointed out by Clausius.

We therefore prove that the force-four-vector on (A) can be put into the Lagrangian forms

$$\left. \begin{aligned} X &= \frac{\partial \Phi}{\partial x} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_1} \right) \\ Y &= \frac{\partial \Phi}{\partial y} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_2} \right) \\ Z &= \frac{\partial \Phi}{\partial z} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_3} \right) \\ L &= \frac{\partial \Phi}{\partial l} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_4} \right) \end{aligned} \right\} \dots\dots (9)$$

Similarly, if R = perpendicular distance of the point B (a, b, c, λ) from the axis of motion of (A) (x, y, z, l), i.e.,

$$R^2 = (x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2 + [(x-a)w_1 + (y-b)w_2 + (z-c)w_3 + (l-\lambda)w_4]^2,$$

and Φ' denotes the expression

$$\frac{\rho\rho_0'}{R'} (w_1w_1' + w_2w_2' + w_3w_3' + w_4w_4'),$$

the forces exerted by A on B are given by the equations

$$\left. \begin{aligned} X' &= \frac{\partial \Phi'}{\partial a} - \frac{d}{d\tau'} \left(\frac{\partial \Phi'}{\partial \omega_1'} \right) & Y' &= \frac{\partial \Phi'}{\partial b} - \frac{d}{d\tau'} \left(\frac{\partial \Phi'}{\partial \omega_2'} \right) \\ Z' &= \frac{\partial \Phi'}{\partial c} - \frac{d}{d\tau'} \left(\frac{\partial \Phi'}{\partial \omega_3'} \right) & L' &= \frac{\partial \Phi'}{\partial \lambda} - \frac{d}{d\tau'} \left(\frac{\partial \Phi'}{\partial \omega_4'} \right) \end{aligned} \right\} (10)$$

8. Two Electrons in Motion.

In the foregoing sections we treated the case of two point-charges. We shall now take the case of two electrons when these are in a state of motion. It will be shown that the same equations would hold if instead of the rest densities ρ_0, ρ_0' , we substitute the invariant charges (e, e') and suppose the whole charge to be concentrated at the centre of each.

The electron occupies the space

$$(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 \leq r^2;$$

where (x, y, z) are the space-components of any point within the electron, (x_0, y_0, z_0) the corresponding quantities for the centre, and r is the radius.

In three-dimensions this equation represents a sphere, but in four-dimensions this represents a spherical cylinder having infinite extension along the time-axis. The equation shows that the electron is at rest.

We shall now write down the equation of a spherical electron moving with a uniform velocity (u_1, u_2, u_3).

In three-dimensions, the equation of a circular cylinder having the line

$$\frac{x-x_0}{l} = \frac{y-y_0}{m} = \frac{z-z_0}{n}$$

as the axis is given by the equation

$$(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 - [l(x-x_0) + m(y-y_0) + n(z-z_0)]^2 = r^2.$$

Similarly, in four-dimensions, since the axis of motion is given by

$$\frac{x-x_0}{i\omega_1} = \frac{y-y_0}{i\omega_2} = \frac{z-z_0}{i\omega_3} = \frac{l-l_0}{i\omega_4},$$

therefore the equation of the cylinder having this as axis is $(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 + (l-l_0)^2 + [w_1(x-x_0) + w_2(y-y_0) + w_3(z-z_0) + w_4(l-l_0)]^2 = r^2$.

That this is so can easily be observed by introducing a Lorentz-transformation in which the line of motion is the new time-axis, and the velocity is equivalent to the moment of transformation. Then if (ξ, η, ζ, ν) be the new co-ordinates, we have

$$\begin{aligned} (\xi-\xi_0)^2 + (\eta-\eta_0)^2 + (\zeta-\zeta_0)^2 + (\nu-\nu_0)^2 \\ = (x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 + (l-l_0)^2 \end{aligned}$$

and

$$i[w_1(x-x_0) + w_2(y-y_0) + w_3(z-z_0) + w_4(l-l_0)] = \nu - \nu_0.$$

$\therefore$ the equation of the electron becomes

$$(\xi-\xi_0)^2 + (\eta-\eta_0)^2 + (\zeta-\zeta_0)^2 = r^2.$$

We shall now calculate the potential-four-vector due to the motion of electron at an external point (a, b, c, λ).

We have

$$\mathbf{a} = \frac{1}{\pi} \iiint \frac{\rho_0(\omega) dx dy dz dl}{[(x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2]}, \quad (10a)$$

the integration being extended over the whole world-space enclosed by the electron.

We shall now introduce again the above-mentioned Lorentz-transformation. Then we can write

$$\begin{aligned} d\xi d\eta d\zeta d\nu \text{ for } dx dy dz dl, \\ \rho_0(0, 0, 0, i) \text{ for } \rho_0(\omega_1, \omega_2, \omega_3, \omega_4), \end{aligned}$$

and $(\xi-\xi')^2 + (\eta-\eta')^2 + (\zeta-\zeta')^2 + (\nu-\nu')^2$ for $(x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2$.

Now $\mathbf{a}'$ the transformed of $\mathbf{a}$ becomes

$$= \frac{1}{\pi} \iiint \frac{\rho_0(0, 0, 0, i) d\xi d\eta d\zeta d\nu}{(\xi-\xi')^2 + (\eta-\eta')^2 + (\zeta-\zeta')^2 + (\nu-\nu')^2},$$

integrated over the world-space

$$(\xi-\xi_0)^2 + (\eta-\eta_0)^2 + (\zeta-\zeta_0)^2 \leq r^2. \quad (\text{A}).$$

We shall first integrate over the new time-axis. The limits are then from $-\infty$ to $+\infty$.

$$\therefore \mathbf{a}' = \iiint \frac{\rho_0(0, 0, 0, i) d\xi d\eta d\zeta}{\sqrt{(\xi-\xi')^2 + (\eta-\eta')^2 + (\zeta-\zeta')^2}},$$

over the spherical volume (A). This is a three-dimensional potential problem, and is easily seen to be

$$= \frac{e(0,0,0,i)}{\sqrt{(\xi_0 - \xi')^2 + (\eta_0 - \eta')^2 + (\zeta_0 - \zeta')^2}},$$

where $e = \iiint \rho_0 d\xi d\eta d\zeta$,

integrated over the spherical volume (A).

Now $\sqrt{(\xi_0 - \xi')^2 + (\eta_0 - \eta')^2 + (\zeta_0 - \zeta')^2}$ is the perpendicular distance from the external point (ξ', η', ζ') on the axis of motion; we can denote this by R .

Then

$$\mathbf{a}' = \frac{(0, 0, 0, i)e}{R}.$$

Now $\mathbf{a}'$ is what the potential-four-vector $\mathbf{a}$ with the components $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4)$ becomes when the transformation is introduced. Retransforming to the original coordinates, we have

$$[\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4] = \frac{(w_1, w_2, w_3, w_4)e}{R} \quad \dots (11)$$

We can now express R in terms of the original system of coordinates.

$$R^2 = (x_0 - a)^2 + (y_0 - b)^2 + (z_0 - c)^2 + (l_0 - \lambda)^2 + [(x_0 - a)w_1 + (y_0 - b)w_2 + (z_0 - c)w_3 + (l_0 - \lambda)w_4]^2,$$

where (x_0, y_0, z_0, l_0) are the coordinates of the centre of the electron, (a, b, c, λ) those of the external point.

N.B. The Scalar and Vector potentials due to the motion of an electron were first obtained by Lienard and Wiechert²⁰ about 1898. They were expressed in the form

$$\phi = \frac{e}{r(1 - u_r/c)}, \quad [F, G, H] = \frac{e}{r(1 - u_r/c)} \left(\frac{u_1}{c}, \frac{u_2}{c}, \frac{u_3}{c} \right), \dots (12)$$

where r is the distance of the external point from the point occupied by the electron at a time $(t - u_r/c)$, etc. (u_1, u_2, u_3) are the velocity components at the time $(t - r/c)$, u_r is the component of this velocity along the line of r .

The expression (11) is in fact equivalent to the expression (12), as the following reasoning will show. Suppose the time-coordinates are so chosen that

$$(x_0 - a)^2 + (y_0 - b)^2 + (z_0 - c)^2 + (l_0 - \lambda)^2 = 0,$$

$$\text{i.e. } c(t_0 - t') = -r,$$

$$\text{or } t = t_0 + \frac{r}{c}.$$

We are in fact estimating the effect at the external point r/c seconds after the electron had been in the position (x_0, y_0, z_0) .

Then, since

$$R^2 = (x - a)^2 + (y - b)^2 + (z - c)^2 + (l - \lambda)^2 + [(x - a)w_1 + (y - b)w_2 + (z - c)w_3 + (l - \lambda)w_4],$$

we can, denoting by R' the four-vector with the components $\{(x - a), (y - b), (z - c), (l - \lambda)\}$,

$$\text{write} \quad R^2 = R'^2 + (R'w)^2,$$

where $(R'w)$ denotes the scalar product of the four-vectors R' and w .

With the above assumption, we have $R' = 0$,

$$\therefore |R| = |(R'w)| = \frac{u_1(x - a) + u_2(y - b) + u_3(z - c) - r}{\sqrt{1 - u^2}},$$

$\therefore$ We can write

$$[\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4] = \frac{e\omega}{(R'w)} = \frac{r}{r(1 - u_r)} [u_1, u_2, u_3, i].$$

Using the ordinary time-coordinate, we have

$$\phi = \frac{e}{r(1 - \frac{u_r}{c})}, \quad \text{F. G. H} = \frac{e(u_1, u_2, u_3)/c}{r(1 - \frac{u_r}{c})} \quad \dots (12)$$

This result has been obtained in various ways by Herglotz²¹, Sommerfeld²², and other workers. Sommerfeld effects the integration of equation (10 a), with the aid of Cauchy's law of residues, and confirms the result (previously obtained by Herglotz),

$$\mathbf{a} = \frac{e\omega}{R'w} \quad \dots (11')$$

But a comparison of the methods of arriving at the two formulae will show that the expression (11') is but a partial statement of the result, it being assumed from the very beginning that the time-coordinates are separated by the interval r/c , where r = three-dimensional distance between

the points. The result $\mathbf{a} = \frac{e\omega}{R}$ is perfectly general, and in full agreement with the requirements and the spirit of the principle of relativity. This reduces to the expression (11'), when for the purpose of forming an idea of the result in three-dimensions, we make the particular assumption just mentioned about the time-coordinates. Hence it is apparent that when we apply the result to the determination of the magnetic and electric forces, and the ponderomotive force, we must use the expression (11), and not (11').

9. The Ponderomotive Force on an Electron due to the field produced by the motion of another electron.

In § 6 we investigated the action of a point-charge on another charge; in the present section we shall investigate the action of an electron (B) [coordinates of centre (a, b, c, λ) , velocity components (v_1, v_2, v_3)] upon another electron A [charge e , coordinates of centre (x, y, z, l) , velocities (u_1, u_2, u_3)].

²¹ Herglotz, *Gött. Nach.* Heft 6. (1940).

²² Sommerfeld, *Ann. d. Physik*, vol. xxxiii. p. 666.

²⁰ L'Eclairage Electrique, vol xvi, 1898; Wiechert, *Ann. d. Physik*, vol. iv.

The components of the ponderomotive force upon a point (x', y', z', l') of the electron A are given by the four components of the matrix

$$\rho_0 \begin{vmatrix} \omega_1 & \omega_2 & \omega_3 & \omega_4 \\ \frac{\partial}{\partial x'} & \frac{\partial}{\partial y'} & \frac{\partial}{\partial z'} & \frac{\partial}{\partial l'} \\ \mathbf{a}'_1 & \mathbf{a}'_2 & \mathbf{a}'_3 & \mathbf{a}'_4 \end{vmatrix},$$

where $\mathbf{a}' = \frac{e' \omega'}{R'}$,

$$R'^2 = (x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2 + [\omega_1'(x-a) + \omega_2'(y-b) + \omega_3'(z-c) + \omega_4'(l-\lambda)]^2,$$

$$\text{and } [\omega_1', \omega_2', \omega_3', \omega_4'] = \frac{1}{\sqrt{(1-v^2)}} [v_1, v_2, v_3, v_4].$$

The total force is obtained by integrating each of these four expressions over the whole volume of the electron A. The X-component of force

$$\rho_0 = \left[\frac{\partial \phi'}{\partial X'} - \frac{d}{d\tau'} \left(\frac{\partial \phi'}{\partial \omega'} \right) \right],$$

where $d\tau' = \sqrt{(1-u^2)} \cdot dt$,

and $\omega_1 = \frac{\partial X'}{\partial \tau} = \frac{\partial X'}{\partial \tau}$,

for all points of the electron move with the same velocity,

and $\phi' = \frac{e'}{R'} [\omega_1 \omega_1' + \omega_2 \omega_2' + \omega_3 \omega_3' + \omega_4 \omega_4']$.

The total force

$$X = \iiint \rho_0 \left[\frac{\partial \phi}{\partial x'} - \frac{d}{d\tau} \left(\frac{\partial \phi}{\partial \omega_1} \right) \right] d\Omega;$$

$d\Omega$ being the contents of the normal section of the cylinder $(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 + (l-l_0)^2 + [x'-x_0]\omega_1 + [y'-y_0]\omega_2 + [z'-z_0]\omega_3 + [l'-l_0]\omega_4]^2 = r^2$. (13)

It can be easily proved that

$$\frac{\partial \phi}{\partial x'} \left(\frac{1}{R'} \right) = \frac{\partial}{\partial x_0} \left(\frac{1}{R} \right)$$

for the points x_0 and x are rigidly connected. Accordingly

$$X = \iiint \left[\rho_0 \left\{ \frac{\partial \phi'}{\partial x_0} - \frac{d}{d\tau} \left(\frac{\partial \phi'}{\partial \omega_1} \right) \right\} \right] d\Omega.$$

Let $\int \rho_0 \phi' d\Omega = \Phi$.

$$\text{Then } X = \frac{\partial \Phi}{\partial x_0} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_1} \right).$$

To evaluate Φ we need only find out the value of the integral

$$I = \iiint \frac{d\Omega}{R'}.$$

Introducing the Lorentz-transformation, in which the axis of motion of the cylinder (13) becomes the new time-axis, we have now

$$I = \iiint \frac{d\xi d\eta d\zeta}{R'}$$

over the volume $(\xi-\xi_0)^2 + (\eta-\eta_0)^2 + (\zeta-\zeta_0)^2 \leq r^2$;

and R' is expressed in terms of the new-coordinate system. Let $(\xi', \eta', \zeta', \nu')$ be the new coordinates of B.

Then

$$R'^2 = (\xi-\xi')^2 + (\eta-\eta')^2 + (\zeta-\zeta')^2 + (\nu-\nu')^2 + [(\xi-\xi')\omega_1'' + (\eta-\eta')\omega_2'' + (\zeta-\zeta')\omega_3'' + (\nu-\nu')\omega_4'']^2,$$

where $(\omega_1'', \omega_2'', \omega_3'', \omega_4'')$ are the direction cosines of the axis of B in the new system. R' is therefore of the form

$$R'^2 = A\xi^2 + B\eta^2 + C\zeta^2 + 2H\xi'\eta' + 2G\eta'\zeta' + 2F\eta'\zeta' + 2U\xi' + 2V\eta' + 2W\zeta' + D.$$

Let (R) be the same function of (ξ_0, η_0, ζ_0) i.e. R is now the perpendicular distance of the centre of A from the axis of B.

Then it can be proved that approximately

$$I = \frac{\Omega}{R} \left[1 - \frac{(2-\omega_4'')}{R} r^2 + \dots \right].$$

Neglecting terms of higher order than the first, we have

$$I = \frac{\Omega}{R}.$$

(In view of the fact that the radius of the electron is extremely small, the second term must be infinitesimal of a higher order compared with the first).

Therefore as a first approximation,

$$\Phi = \frac{ee'}{R} (\omega_1 \omega_1' + \omega_2 \omega_2' + \omega_3 \omega_3' + \omega_4 \omega_4').$$

$$\therefore \left. \begin{aligned} X &= \frac{\partial \Phi}{\partial x} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_1} \right) \\ Y &= \frac{\partial \Phi}{\partial y} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_2} \right) \\ Z &= \frac{\partial \Phi}{\partial z} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_3} \right) \\ L &= \frac{\partial \Phi}{\partial l} - \frac{d}{d\tau} \left(\frac{\partial \Phi}{\partial \omega_4} \right) \end{aligned} \right\} \dots \dots \dots (14)$$

dropping the subscripts 0, (x, y, z, l) now denoting the coordinates of the centre.

10. Laws of Electrodynamical Action.

We shall now reduce the Lagrangian function to three-dimensions. We have

$$\Phi = \frac{ee'(\omega_1 \omega_1' - \omega_2 \omega_2' + \omega_3 \omega_3' + \omega_4 \omega_4')}{\{(x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2 + [(x-a)\omega_1' + \dots]^2\}^{\frac{1}{2}}}$$

Putting $(x-a)^2 + (y-b)^2 + (z-c)^2 + (l-\lambda)^2 = 0$

just as we did in the interpretation of the potential-four-vector, we have

$$\Phi = \frac{ee'(u_1 v_1 + u_2 v_2 + u_3 v_3 - 1)}{r(1-v_r) \sqrt{(1-u^2)}} \dots \dots (15)$$

with the same interpretation for r and v_r as before.

Excepting for the factor $[(1-v_r)\sqrt{(1-u^2)}]$ in the denominator, the form for P is identical with that assumed by Clausius for explaining the laws of electrodynamic action. The occurrence of these terms need not cause us any

confusion; following in the wake of Clausius, we can easily prove that this formula leads to the laws of electrodynamical action just as well as any one of the formulae mentioned in the introduction. We have to take terms up to the second order, and instead of using r , we shall have to introduce the instantaneous distance r' which differs from $r(1-v_r)$ by terms of second order only. The second order terms arising out of $r(1-v_r)$ and $\sqrt{(1-u^2)}$ affect only one electron; while the term $(u_1v_1+u_2v_2+u_3v_3)$ affects both of them. Remembering that current consists of equal quantities of positive and negative charges moving in opposite directions, there will be no difficulty in realizing that in the final process of summation, terms affecting only one electron would cancel out, and only terms involving both of the electrons would remain in the final result. For further particulars, I would refer the reader to the above-mentioned memoir of Clausius's where the whole thing is worked out in a most elaborate and convincing manner.

11.

While the main object which I had in view when the work was undertaken has been achieved, viz., the deduction of the laws of electrodynamical action between two closed currents from the theory of electrons, I wish to point out certain other consequences to which this investigation may lead. With the help of Minkowski's four-dimensional analysis, I have succeeded in recasting the important result of Lienard and Wiechert (on the field produced by a moving electron) in an entirely novel form, and as I believe the only form consistent with the principle of relativity. The potential-four-vector has been proved to be equivalent to $(e\omega/R)$, where e =total charge, ω =velocity-four-vector of the electron, and R is the four-dimensional perpendicular distance of the external point from the axis of motion of the electron. By applying the theorem in this simple form to Lorentz's equations for the ponderomotive force acting on an electron, it has been found possible to deduce a Lagrangian function controlling the motion of two electrons round each other. It has been shown that for small velocities, the result is practically identical with that tentatively assumed by Clausius in 1880 for explaining the laws of electrodynamical action on the atomistic hypothesis. There is one important distinction to which attention should be drawn.

In the usual form of Lagrangian equations of motion, we express the force X in the form

$$X = \frac{\partial \phi}{\partial x} - \frac{d}{d\tau} \left(\frac{\partial \phi}{\partial \dot{x}} \right).$$

But here we have

$$X = \frac{\partial \phi}{\partial x} - \frac{d}{d\tau} \left(\frac{\partial \phi}{\partial \dot{x}} \right),$$

i.e. in place of time t , we have to use the proper-time τ , where $d\tau = \sqrt{(1-u^2)} dt$.

The name proper-time for the function τ , suggests that it has some special relation with the time-coordinate, whereas in fact it is perfectly symmetrical, and similarly related to each of the four coordinates. To dispel any such false notion, it is now usual to designate $d\tau$ as an element of length of the world-line of motion. Thus

$$d\tau = ds = \sqrt{dt^2 - dx^2 - dy^2 - dz^2},$$

and $(\omega_1, \omega_2, \omega_3, \omega_4)$ becomes $\sqrt{-1}$ times the direction cosines of the element dS .

In a system consisting of two electrons only, the forces controlling the motion are due to electronic attraction only; the gravitational field, being 10^{-42} times smaller than the electronic field, can be entirely neglected. Following Minkowski,²³ the equations of motion can be written in the forms:

$$\left. \begin{aligned} c^2 m_0 \frac{d^2 x}{ds^2} &= \frac{\partial \phi}{\partial x} - \frac{d}{ds} \left(\frac{\partial \phi}{\partial \dot{x}} \right) \\ c^2 m_0 \frac{d^2 y}{ds^2} &= \frac{\partial \phi}{\partial y} - \frac{d}{ds} \left(\frac{\partial \phi}{\partial \dot{y}} \right) \\ c^2 m_0 \frac{d^2 z}{ds^2} &= \frac{\partial \phi}{\partial z} - \frac{d}{ds} \left(\frac{\partial \phi}{\partial \dot{z}} \right) \\ c^2 m_0 \frac{d^2 l}{ds^2} &= \frac{\partial \phi}{\partial l} - \frac{d}{ds} \left(\frac{\partial \phi}{\partial \dot{l}} \right) \end{aligned} \right\} \left. \begin{aligned} m' \frac{d^2 a}{ds'^2} &= \frac{\partial \phi'}{\partial a} - \frac{d}{ds'} \left(\frac{\partial \phi'}{\partial \dot{a}} \right) \\ m' \frac{d^2 b}{ds'^2} &= \frac{\partial \phi'}{\partial b} - \frac{d}{ds'} \left(\frac{\partial \phi'}{\partial \dot{b}} \right) \\ m' \frac{d^2 c}{ds'^2} &= \frac{\partial \phi'}{\partial c} - \frac{d}{ds'} \left(\frac{\partial \phi'}{\partial \dot{c}} \right) \\ m' \frac{d^2 \lambda}{ds'^2} &= \frac{\partial \phi'}{\partial \lambda} - \frac{d}{ds'} \left(\frac{\partial \phi'}{\partial \dot{\lambda}} \right) \end{aligned} \right\} \dots (16)$$

These equations are a particular case of the general equations of motion of an electron

$$\left. \begin{aligned} \frac{m_0 c^2}{e} \frac{d^2 x}{d\tau^2} &= \omega_2 f_{12} + \omega_3 f_{13} + \omega_4 f_{14} \\ \frac{m_0 c^2}{e} \frac{d^2 y}{d\tau^2} &= \omega_1 f_{21} + \omega_3 f_{23} + \omega_4 f_{24} \\ \frac{m_0 c^2}{e} \frac{d^2 z}{d\tau^2} &= \omega_1 f_{31} + \omega_2 f_{32} + \omega_4 f_{34} \\ \frac{m_0 c^2}{e} \frac{d^2 l}{d\tau^2} &= \omega_1 f_{41} + \omega_2 f_{42} + \omega_3 f_{43} \end{aligned} \right\} \dots (17)$$

These equations can be deduced from the Principle of Least Action in the following manner. The ordinary form of the Principle of Least Action is

$$\delta \int (T - V) dt = 0 \dots (18)$$

Instead of dt we write $d\tau = \sqrt{dt^2 - dx^2 - dy^2 - dz^2}$, and for T we write $m_0 c^2$, where m_0 =rest-mass of the electron.

We have then

$$\delta V = X\delta x + Y\delta y + Z\delta z + L\delta l,$$

where (X, Y, Z, L) are the components of the Ponderomotive

²³ Minkowski, loc. cit. Appendix.

Force-four-vector, $(\delta x, \delta y, \delta z, \delta l)$ are the variational displacements.

Instead of the ordinary form, we have now

$$\delta \int m_0 c^2 d\tau - \int \delta V d\tau = 0 \quad \dots (18')$$

Now $d\tau = -(\omega_1 dx + \omega_2 dy + \omega_3 dz + \omega_4 dl)$,

and $\delta V d\tau = -[X\delta x + Y\delta y + Z\delta z + L\delta l] ds$

$$= -e[f_{12}(\delta x dy - dx \delta y) + f_{23}(\delta y dz - dy \delta z) + f_{31}(\delta z dx - dz \delta x) + f_{14}(\delta x dl - dx \delta l) + f_{24}(\delta y dl - dy \delta l) + f_{34}(\delta z dl - dz \delta l)].$$

Now we shall prove an auxiliary theorem²⁴; the (X, Y, Z, L) used in this proof have no connexion with the force-components.

We have

$$\begin{aligned} & \int X dx + Y dy + Z dz + L dl \\ &= \int X \delta x + \int X \delta dx \\ &= \sum \int \left(\frac{\partial X}{\partial x} \delta x + \frac{\partial X}{\partial y} \delta y + \frac{\partial X}{\partial z} \delta z + \frac{\partial X}{\partial l} \delta l \right) dx + \\ & \quad + \sum \int \left[X \left(\frac{\partial \delta x}{\partial x} dx + \frac{\partial \delta x}{\partial y} dy + \frac{\partial \delta x}{\partial z} dz + \frac{\partial \delta x}{\partial l} dl \right) \right]. \end{aligned}$$

After partial integration, the second term equals

$$\sum X \delta x \Big|_{\text{final}}^{\text{initial}} - \sum \int \left(\frac{\partial X}{\partial x} dx + \frac{\partial X}{\partial y} dy + \frac{\partial X}{\partial z} dz + \frac{\partial X}{\partial l} dl \right) \delta x.$$

Hence $\delta \int X dx + Y dy + Z dz + L dl$

$$= X \delta x + Y \delta y + Z \delta z + L \delta l \Big|_{\text{final}}^{\text{initial}} + \int \left(\frac{\partial Y}{\partial x} - \frac{\partial X}{\partial y} \right)$$

$$(\delta x dy - dx \delta y) + 5 \text{ other similar terms.}$$

Now for (X, Y, Z, L) substitute $m_0 c^2 (\omega_1, \omega_2, \omega_3, \omega_4)$ and let us denote

$$\left(\frac{\partial \omega_k}{\partial x_h} - \frac{\partial \omega_h}{\partial x_k} \right) \text{ by } \Omega_{hk}.$$

Then we have

$$\begin{aligned} \delta \int m_0 c^2 ds &= \delta \int m_0 c^2 (\omega_1 dx + \omega_2 dy + \omega_3 dz + \omega_4 dl) \\ &= m_0 c^2 (\omega_1 \delta x + \omega_2 \delta y + \omega_3 \delta z + \omega_4 \delta l) \Big|_{\text{final}}^{\text{initial}} \end{aligned}$$

$$+ \int [\Omega_{12}(\delta x dy - dx \delta y) + \Omega_{23}(\delta y dz - dy \delta z) + \Omega_{31}(\delta z dx - dz \delta x) + \Omega_{14}(\delta x dl - dx \delta l) + \Omega_{24}(\delta y dl - dy \delta l) + \Omega_{34}(\delta z dl - dz \delta l)].$$

Putting the first term = 0 as usual, we have from equation (18')

$$\int [(m_0 c^2 \Omega_{12} + e f_{12})(\delta x dy - dx \delta y) + 5 \text{ other similar terms}] = 0.$$

The six-components of the six-vector $(\delta s \times ds)$ are not independent, hence we cannot put their coefficients

individually = 0. If this were possible we would have obtained the system of equations

$$-\frac{m_0 c^2}{e} = \frac{f_{12}}{\Omega_{12}} = \frac{f_{23}}{\Omega_{23}} = \frac{f_{31}}{\Omega_{31}} = \frac{f_{14}}{\Omega_{14}} = \frac{f_{24}}{\Omega_{24}} = \frac{f_{34}}{\Omega_{34}},$$

since (dx, dy, dz, dl) represent the actual displacement, $(\delta x, \delta y, \delta z, \delta l)$ the variational displacements.

We shall have to collect the coefficients of $(\delta x, \delta y, \delta z, \delta l)$ separately and put them individually equal to zero. In this way we obtain the four equations

$$\left. \begin{aligned} -\frac{m_0 c^2}{e} &= \frac{f_{12}\omega_2 + f_{13}\omega_3 + f_{14}\omega_4}{\Omega_{12}\omega_2 + \Omega_{13}\omega_3 + \Omega_{14}\omega_4} = \frac{f_{21}\omega_1 + f_{23}\omega_3 + f_{24}\omega_4}{\Omega_{21}\omega_1 + \Omega_{23}\omega_3 + \Omega_{24}\omega_4} \\ &= \frac{f_{31}\omega_1 + f_{32}\omega_2 + f_{34}\omega_4}{\Omega_{31}\omega_1 + \Omega_{32}\omega_2 + \Omega_{34}\omega_4} = \frac{f_{41}\omega_1 + f_{42}\omega_2 + f_{43}\omega_3}{\Omega_{41}\omega_1 + \Omega_{42}\omega_2 + \Omega_{43}\omega_3} \end{aligned} \right\} \quad (17')$$

Of these, only three are independent.

It is easy to see that

$$m_0 c^2 [\omega_2 \Omega_{12} + \omega_3 \Omega_{13} + \omega_4 \Omega_{14}] = m_0 c^2 \frac{d^2 x}{ds^2},$$

$$\begin{aligned} \text{for } \omega_2 \Omega_{12} + \omega_3 \Omega_{13} + \omega_4 \Omega_{14} &= \omega_2 \left(\frac{\partial \omega_2}{\partial x} - \frac{\partial \omega_1}{\partial y} \right) \\ &+ \omega_3 \left(\frac{\partial \omega_3}{\partial x} - \frac{\partial \omega_1}{\partial z} \right) + \omega_4 \left(\frac{\partial \omega_4}{\partial x} - \frac{\partial \omega_1}{\partial l} \right) \\ &= \frac{\partial}{\partial x} [\omega_1^2 \times \omega_2^2 + \omega_3^2 + \omega_4^2] \\ &- \left(\omega_1 \frac{\partial}{\partial x} + \omega_2 \frac{\partial}{\partial y} + \omega_3 \frac{\partial}{\partial z} + \omega_4 \frac{\partial}{\partial l} \right) \omega_1 \\ &= -\frac{d\omega_1}{ds} = -\frac{d^2 x}{ds^2} \end{aligned}$$

for $\omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2 = -1$, $\therefore$ the first term = 0.

The system of equations (17') are thus practically identical with the equations (17) but for practical purposes this form may be more convenient than the Minkowskian form.

The six-vector Ω may be styled as the "acceleration" six-vector, $(\Omega_{23}, \Omega_{31}, \Omega_{12})$ being connected with the three components of rotation, and $(\Omega_{14}, \Omega_{24}, \Omega_{34})$ with the three components of acceleration

$$\left(\frac{d^2 x}{dt^2}, \frac{d^2 y}{dt^2}, \frac{d^2 z}{dt^2} \right).$$

In conclusion, I wish to express my thanks to Prof. D. N. Mallik, and my friend Mr. Satyendra Nath Basu for their kind help and encouragement.²⁵

²⁵ The paper was communicated about two years ago, but owing to irregularities of the mail service caused by the war, the publication has been rather delayed. Meanwhile much work has been published on the subject, especially several important papers by Crehore in the 'Physical Review'. The author takes this opportunity of expressing his regret that he has not been able to compare his results with those obtained by Crehore and other workers.

²⁴ Vide Cunningham, Principle of Relativity, Chap VIII.

10. ON SELECTIVE RADIATION PRESSURE AND THE RADIATIVE EQUILIBRIUM OF THE SOLAR ATMOSPHERE

(Jour. Dept. Science, Calcutta University, 2 (Physics), 51, 1920)

§1

In a paper recently communicated to the *Astrophysical Journal*, an attempt has been made to prove that the quantum theory affords a basis for the existence of radiation-pressure on atoms and molecules.¹ It is well-known that according to the older continuous theory, the pressure of light is evanescent, on obstacles of the atomic or molecular size. But this conclusion is contrary not only to the requirements of many astrophysical data, but also to the experimental results of Lebedew.² In some recent communications to the M. N. R. A. S., and the *Astrophysical Journal*, Professor Eddington³ has developed a very elegant theory on the "Radiative Equilibrium in the interior of stars," and has successfully explained many of the observational results about the evolution of stars discovered by Russell,⁴ Hertzsprung and others. The theory of Eddington is based on the assumption of the existence of radiation-pressure on atoms. We may just quote his own words.⁵

"As there seems to be a rather widespread impression that gases are not subject to radiation-pressure, it may be advisable to state the theory briefly. The pressure is simply a consequence of absorption or scattering. A beam of radiation carries a certain forward-momentum proportional to its intensity, after passing through a sheet of absorbing medium, a weaker beam emerges carrying proportionately less momentum: the difference of incident and emergent momentum is retained by the medium and constitutes the pressure. The medium, in fact, absorbs the momentum of the beams in the same proportion as it absorbs the energy. The calculations of radiation-pressure on small solid particles are simply calculations of absorption and scattering by these particles; it is not possible to apply such methods to atoms and molecules, which absorb by some internal mechanism. But the relation between absorption and pressure is a perfectly general one, depending only on the conservation of momentum."

In the paper mentioned above, I have tried to prove that the existence of radiation-pressure on gaseous atoms

follows as an easy deduction from modern theories of emission and absorption. *It has also been suggested that the action of light pressure is selective.* Let us consider in greater detail what is meant by this term. Suppose a continuous spectrum from a bright back-ground passes through a layer of gas. Then the gaseous atoms will be acted upon by only those pulses of light in the continuous spectrum, which the gas is itself capable of emitting and absorbing. If, for example, the gas be composed of Sodium atoms; then only radiant energy contained in the spectral regions about the D_1 , D_2 -lines and sometimes the other lines of the principal series will act upon the Na-atoms. The remaining part of the continuous light will be without action on the Na-atoms (more later on). Regarded from this point of view, the theory may properly be styled *as the theory of Selective Radiation-pressure*. The object of the present paper is to show that this theory taken along with the modern theories of atomic structure, is capable of explaining many problems in solar and stellar physics, particularly the problems of the radiative equilibrium of the solar atmosphere.

The range of phenomena covered by the works of Eddington is entirely different from ours. Eddington has considered the aggregate effect of light pressure in the interior of stars, *i.e.*, the region where the gaseous atoms are under such a high pressure that they no longer emit, or absorb waves of a particular type, but waves of all lengths. The mass of gas behaves very much like a continuous body, and the radiation pressure is just the same as that given by the continuous theory, for only the aggregate effect is considered. But the class of phenomena which will be discussed in this article refers to the atmospheres of luminous bodies, where the pressure is so low that the gaseous atoms are capable of emitting their own characteristic radiation. The general problem of radiative equilibrium has already been discussed by Schwarzschild.⁶ Before taking up these discussions, I shall give a brief sketch of the problems before us.

§ 2. The Problems of the Solar Atmosphere.

It is well known that the customary division of the sun into the photosphere, the reversing layer, and the

¹ M. N. Saha, *Astrophysical Journal*, 1919.

² Lebedew—*Annalen der Physik*, Vol. 32, p. 411 (1910).

³ Eddington—M. N. R. A. S., Vol. 77, p. 25; *Astrophysical Journal*, Vol. 46.

⁴ Russell—*Nature*, Vol. 93.

⁵ Eddington—M. N. R. A. S., Vol. 79, p. 28, *et seq.*

⁶ Schwarzschild—*Gött Nachrichten*, 1906, p. 41.

chromosphere is based upon the results of spectroscopic observations alone. The correlation of these data to actual physical conditions of temperature, pressure, and distribution of mass is a rather tough problem, and one may find in this connection views which are poles asunder. When we speak of the photosphere, we tacitly assume it to be a sharply defined body like a piece of white-hot iron. The reversing layer and the chromospheres are assumed to be similar to the lower and the upper layers of our own atmosphere. In the discussion which follows, we stick to the view that the photosphere has a sharp, though gaseous boundary, and radiates like a black body at a temperature of 7600°K .⁷

The problems may be briefly grouped under the following headings:—

(1) The enormous distance to which the atmosphere extends over the photospheric disc.

(2) The anomalous distribution of elements in the solar atmosphere.

(3) The radiating power of the different parts of the solar disc.

(4) Unsteady phenomena, *viz.*, Spots and prominences.

The main points of the first problem are very well-known. The value of the gravitational acceleration on the disc of the sun is 27.7 times the value of gravity on the earth, while the temperature is nearly 6000°K . The radial gradient of the density (*i.e.*, rate of decrement of mass per unit volume with height) should therefore be very large, no matter in whatsoever way the temperature may vary in the atmosphere. Let us consider in succession, the three theories of equilibrium.⁸

(1) The Isothermal Equilibrium:—Temperature is supposed to be uniform throughout the atmosphere and equal to 6000°K .

Let N_0 =number of atoms of a certain element per unit volume just over the photospheric disc, and N =corresponding number at a height z . Then

$$\ln \left(\frac{N}{N_0} \right) = \frac{Mgz}{k\theta} = \frac{mgz}{R\theta} \quad (1)$$

Where R =gas constant= 8.30×10^7 , k =Boltzmann's gas constant, M =weight of an atom, m =weight of a gram-atom, θ =Absolute temperature.

Taking $\theta=6000^\circ\text{K}$, $g=27.7 \times 981 \text{ cm}$, the logarithmic decrement is $\frac{27.7}{6000} \times \frac{1}{300} = \frac{27}{20}$ times the value of the corresponding quantity on the earth. In the case of the Hydrogen atom the density reduces to $\frac{1}{10}$ of its value for a height of 393 km.; for Calcium the corresponding height is only 10 kms. At a height of 1000 kms., the density of Calcium

$\rho = \rho_0 \left(10^{-100} \right)$. ρ_0 =density on the photosphere, *i.e.*, there

will be found scarcely one molecule in the whole volume over the disc. Generally $\rho = \rho_0 \times 10^{-\frac{mz}{\theta}}$, m =atomic weight, z =height in kilometres.

(2) Let us suppose that the temperature does not remain constant, but vary according to the law of adiabatic compression and rarefaction. This will be the case when the atmosphere is the seat of very violent, and turbulent motion, as is the case, to a smaller extent, in the lower atmosphere of the earth (the troposphere). Probably for the lower reversing layer, and the photosphere, the adiabatic law holds good.

The equation of state is

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0} \right)^\gamma - \left(\frac{\theta}{\theta_0} \right)^{\frac{\gamma}{\gamma-1}} \quad (2)$$

γ =ratio between the specific heats; from (1), we have

$$\theta - \theta_0 = \frac{\gamma-1}{\gamma} \frac{Mg}{k} (z - z_0)$$

Taking $\gamma=1.66$, the temperatures should fall by 1°C , for every 70 metres of Hydrogen. The atmosphere has a definite limit ($t=P=\rho=0$). This limit is 420 km. for Hydrogen and 10.5 for Calcium.

(3) The adiabatic equilibrium can take place only in the regions of violent motion. In the upper regions, convection currents are almost absent (except for such occasional outbursts known as the prominences), and the exchange of heat can take place only by radiation.

The theory of radiative equilibrium is due to Schwarzschild. It is based upon Kirchhoff's laws of emission and absorption, and primarily deals with the problem of variation of temperature with height and the darkening of the solar disc towards the edge. It is noteworthy that Schwarzschild does not attempt to account for either the great extension of the solar atmosphere or the anomalous distribution of elements. This is due to the fact that following the old continuous theory he regards the atoms and molecules as infinitely small fragments of black body, and finds the radiation pressure to be evanescent on them.⁹

The arguments of Schwarzschild may be greatly simplified by following a method due to Fabry¹⁰. Fabry has shown that at any point of free space, traversed by radiation, the motion of temperature has no meaning in itself. Bodies having different physical properties will rise to different temperatures, varying within very wide limits¹¹.

Suppose we have a spherical black body at a height ' z ' over the photospheric disc, and let us suppose that the solar atmosphere has been somehow lifted up. Equilibrium will be established when the heat radiated by the body will be equivalent to the heat received. Let θ_0 =temperature

⁷ Feliz Biscoe, *Astrophysical Journal*, Vol. 46, p. 355 (1917)

⁸ Most of this discussion is taken from Schwarzschild's paper referred to above, and a paper by D. Brunt, M. N. R.A. S., Vol. 72.

⁹ Schwarzschild:—Münchener Berichte—1909.

¹⁰ Fabry, *Astrophysical Journal*, Vol. 47.

¹¹ The maximum temperature must, however, be less than the temperature of the radiating body.

of the disc, θ =temperature of the body. Then according to Stefan's law we have

$$\theta = \theta_0 \left(\frac{\Omega}{4\pi} \right)^{\frac{1}{4}},$$

where Ω =solid angle subtended by the body at the sun,
 $= 2\pi \left(1 - \frac{2z}{r} \right)$ approximately,
 $= 2\pi$,

when z is very small. The value of z being generally very small in comparison to r , the radius (the maximum value of $\frac{z}{r} = \frac{14000}{7 \times 10^5} = \frac{1}{50}$ in the case of the H-K lines), the above assumption is quite justified.

Let us now see how far the actual conditions in the sun differ from these assumptions. F. Biscoe¹² has recently discussed the vast amount of data collected by the Smithsonian Astrophysical Laboratory on the distribution of intensity for different wave-lengths from different parts of the solar disc. He finds that the photosphere radiates like a black body at a temperature of 7500°K. The discussion of course, refers to those parts of the solar spectrum which contain no strong absorption lines. To account for the Fraunhofer lines, we have to assume that the photosphere is bounded by concentric spherical layers of radiant gas, the temperature gradually decreasing with height. These gases pick out and absorb from the continuous spectrum those pulses which they themselves are capable of emitting, so that these regions of absorption appear relatively dark. The intensity of the dark regions corresponds to the intensity of the outermost layers of the emitting and absorbing gas.

If we suppose that a small spherical black body is placed at a point within the solar atmosphere, the radiation received by it is composed of (1) the radiation from the photosphere attenuated by scattering and general absorption; (2) radiation from the radiant gas of the solar atmosphere interior to the body; (3) radiation from the radiant gas exterior to the body.

Schwarzschild¹³ finds that the combined radiation from the first two causes may be put equivalent to $\sigma\theta'_0{}^4$ where θ'_0 is called the effective temperature. The radiation from the layers exterior to the body $= \int_{-\infty}^z E\rho\epsilon dz$, where E =volume-emission per unit mass, ϵ =absorption per unit mass.

The integral is equal to

$$= \sigma\theta'_0{}^4 \frac{\epsilon}{g} \int_{-\infty}^z \rho g dz = \sigma\theta'_0{}^4 \frac{p}{g}.$$

Hence $2\sigma\theta^4 = \sigma\theta'_0{}^4 \left[1 + \frac{\epsilon}{g} p \right]$, σ =Stefan-constant.

$$\theta = \frac{\theta'_0}{2^{1/4}} \left(1 + \frac{\epsilon}{g} p \right)^{1/4} = \tau \left(1 + \frac{\epsilon}{g} p \right)^{1/4}$$

These assumptions and calculations are very rough. With the aid of this relation between temperature, and pressure, we can easily calculate the density. We have

$$z = \frac{k}{Mg} \int \frac{4\theta^4 d\theta}{\theta^4 - \tau^4} = \frac{k}{Mg} \left[4 \frac{\theta}{\tau} + \log \frac{\theta - \tau}{\theta + \tau} - 2 \tan^{-1} \frac{\theta}{\tau} + \text{const} \right],$$

$$\text{and } \rho = \frac{p}{R\theta} = \frac{g}{R\epsilon} \left(\frac{\theta^4 - \tau^4}{\theta\tau^4} \right)$$

Brunt¹⁴ has calculated the variation of temperature and density with height on the basis of the above formulae; the figures are reproduced below:—

z in km.	z in angular measure	θ	$\theta - \tau$	ρ .
∞	∞	5050°K= τ	0	0
2.1×10^5	5'	„	0	10^{-1636}
4.2×10^4	1'	„	0	10^{-3351}
3.5×10^4	.5"	„	0	10^{-34}
3.97×10^3	.5"	5051	1	3×10^{-6}
2.75×10^2	.4"	5060	10	3×10^{-5}
0		6000	950	3×10^{-3}

This table shows that Schwarzschild's theory leads to an incomprehensible atmosphere with uniform temperature. At a height of 3500 km., where according to the evidence of flash-spectra, lines of H₂, Ca, Fe... are quite plentiful, we obtain a density of 10^{-34} , or only one molecule of Hydrogen in 10^{15} cc of the gas. Schwarzschild's theory therefore fails to account for the great extension of the solar atmosphere.

For a more rigorous application of these formulae we require more precise information about the pressure, and rate of variation of pressure in the photospheric level, and in the reversing layer, as well as the distribution of elements in these levels (*i.e.*, number of atoms of a particular kind per unit volume). The level attained by an element is generally obtained from the length of the arc of the characteristic line of the element in the flash spectrum¹⁵. Now this level is generally different for different lines (*vide* Sec. 4) of the same element. Apart from this difficulty, we have to remember that no conclusion is possible about the minimum radiation density¹⁶ of an element from the chromospheric level alone, unless our knowledge is supplemented by auxiliary laboratory experiments. These points will be further considered in the next section. But from what has been said, it is quite clear that none of the three theories sketched above can account for the observed extension of the solar atmosphere.

It seems to be the general opinion of the astrophysicists that there is some sort of repulsive force on the sun which

¹⁴ Monthly Notices, R. A. S., Vol. 73.

¹⁵ Mitchell—*Astrophysical Journal* Vol. 38, December.

¹⁶ Minimum radiation-density—The minimum number of radiating particles per unit volume which is required for affecting the photographic plate within a certain interval.

¹² F. Biscoe—*Astro. Journal*, Vol. 46 (1917).

¹³ Schwarzschild—*Loc. cit.*

neutralizes the greater part of gravity. It is also supposed that the prominences, particularly, the eruptive ones, are due to some cause which enables "this force of levity" to overcome largely, and in the case of eruptive ones, to preponderate over the force of gravitational attraction on the Sun. We quote the opinions of two distinguished astrophysicists in this connection.

"The rising prominences in some cases observed at Kodaikanal move with an accelerating velocity to be driven entirely away into space by a force opposed to gravity."

(Evershed, *Astrophysical Journal*, Vol. 28, p. 79).

Professor Julius, whose views about the interpretation of astrophysical phenomena are so radically different from those of Evershed, writes in a similar strain:—(*Astrophysical Journal*, Vol. 38, p. 132).

"From the astrophysical point of view, one of the questions material to the explanation of solar phenomena is: What can be presumed about the *general radial gradient of the density in the layers* we are concerned with ?

The subject has been treated very fully and ingeniously on the basis of thermodynamics by Emden in his book 'The Gas-Kugeln'. Emden arrives at the conclusion already mentioned above that the fall of the density must be extremely rapid, but the inference is open to doubt, for in his calculations, Emden presupposes gravitation to be the only radial force acting on solar matter. According to the present state of our physical knowledge, however, we decidedly must admit that *on the sun, gravitation is counteracted by the pressure of radiation*, and by the emission of electrons, and perhaps of other charged particles.

Basing on purely theoretical grounds an estimate of the intensity of that counteraction would, for the present, be as rash as denying its existence; but some evidence in favour of its essentiality is given by the fact that many solar phenomena are much better understood if we assume a radial gradient many times smaller than the one that would correspond to gravitational conditions only. In this

connection we call attention to the puzzling properties of quiescent, hovering prominences. Father Fenyi, in his interesting discussion of the long series of prominence observations made at the Haynald Observatory, Kalosca, is very positive in his assertion that "several well-established facts concerning quiet prominences can be accounted for only if in the solar atmosphere gravity is reduced by *certain repulsive forces to a small fraction (something of the order of 1/80) of its commonly accepted value.*"

In the papers¹⁷ already referred to, Eddington has calculated the compensation of gravity due to radiation-pressure in the interior of a star of given mass, average density, and luminosity. If G denotes, the acceleration due to gravitational attraction alone, and γG the repulsive acceleration due to radiation-pressure, the effective value of gravity reduces to $(1 - \gamma) G$. For a star of the size and mass of the sun, Eddington calculates that $\gamma = .106$, for a molecule of weight 2, and .943 for a molecule of weight 54, so that the effective values of gravity in the interior are .894 G for H_2 , and .057 G for a molecule of weight 54. But as we shall see later on, these calculations apply only to the interior of the star. In the atmosphere, quite a different procedure is to be adopted.

The origin of the "force of levity" has been looked for in two other directions excepting radiation pressure—viz., (1) the existence of electrical forces, (2) diminution of gravitational attraction with temperature. There is not much theoretical or experimental investigation to support the second case, while the first case is rather obscure and problematic. Radiation-pressure has been so long at a 'discount' because relying upon the deductions of the continuous theory, we had to admit that it was evanescent on particles of the atomic size. But if the views presented in my paper already referred to be found acceptable, this objection can no longer be held as valid.

¹⁷ Eddington, M. N. R. A. S., Vol. 77, pp. 16 and 596.

11. NOTE ON THE SECONDARY SPECTRUM OF HYDROGEN*

(*Phil. Mag., Sr. VI, 40, 159, 1920*)

In recent years the problem of the Secondary Spectrum¹ of hydrogen has again come to the forefront, on account of the interest which attaches to it with regard to Bohr's theory of quantum emission of spectral lines. Theoretical physicists are inclined to ascribe the Secondary Spectrum to the molecule of hydrogen, the Primary Spectrum being due to the atom. On the other hand, many experimental physicists are by no means satisfied by the explanation offered, but on the basis of the experiments of Fabry and Buisson², the opinion is sometimes expressed that at least a part of the secondary spectrum may be due to the H-atom.

But a closer perusal of the above-mentioned works of Fabry and Buisson shows that probably proper interpretation has not been put on their experimental results. In their experiments the mass of the radiation centres was calculated from the limit of visibility of the line in question in the Fabry-Perot interferometer according to the formula

$$\frac{\Delta}{\lambda} = A \sqrt{\frac{M}{\theta}},$$

where Δ =limit of visibility, M =weight of the radiating centre in terms of the H-atom as unity, θ =absolute temperature, A is a constant.

Fabry and Buisson found that for the red line $H_\alpha = 6563$, $\frac{D}{\lambda} = 50,000$, while for a secondary line (not mentioned) $\frac{D}{\lambda} = 72,000$.

The value of A was taken from theoretical papers by Lord Rayleigh³ and Schönrock.⁴ Thus they obtained $M=1$ for the secondary line (approximately), but a much smaller value—probably (.5)—for the H_α line.

Since the second value is impossible, they concluded that in both cases $M=1$, the value of Δ for H_α being considered unreliable, because H_α is a double line, and it is rather difficult to determine its limit of interference.

But it has been shown in a paper published in the Physical Review⁵ that the value of A is subject to fluctuations depending upon the silvering of the mirrors, the definition of visibility and other causes. In the papers of Lord Rayleigh and Schönrock the value of A is calculated from two interfering beams only, while in the Fabry-Perot apparatus

we have to do with an infinite number of interfering beams. Hence no absolute reliance can be placed upon a theoretically deduced value of A .

Since for a certain particular apparatus A has a definite value, the best interpretation of Fabry-Perot and Buisson's results seems to be the relative estimation of the masses of the radiating centres in the two cases. We thus have

$$\sqrt{\frac{M_2}{M_1}} = \frac{72,000}{50,000} = 1.4 \text{ or } M_2 = 2M_1 \text{ (approximately);}$$

i.e., the mass of the radiating centres responsible for the emission of a secondary line is twice the mass of the radiating centres emitting H_α . In other words, according to the interpretation given here, the experiments prove the contrary of what is generally deduced from them—viz., if the H_α -line is emitted by an H atom, the secondary lines are emitted by the H molecule.

It is to be hoped that the problem may again be experimentally attacked.

On the theoretical side the difficulty is not only mathematical, but also physical. We have not as yet any mechanical model before us visualizing in a satisfactory manner the coupling of two Bohr atoms into an H-molecule. In the Bohr-Debye model the individuality of the component atoms is entirely lost⁶. This is a serious theoretical objection which has not yet been overcome.

Nicholson⁷ has already calculated, on the basis of Bohr's theory, the radiation from a Bohr model, consisting of a single nucleus and two electrons. But none of the calculated lines agree with any of the observed secondary lines.

I tried to calculate the radiation from a system consisting of two fixed positive centres⁸, and one electron, on the lines of Sommerfeld's generalisation of Bohr's theory. It would give, it was expected, the radiation from a positively charged H-atom. The complete mathematical solution of this problem has already been given by Jacobi⁹. The quanta-integrals come out in terms of elliptic integrals of the first, second, and third kind, but it has not yet been found possible to extricate the energy out of these functions, and express it in terms of the quanta-numbers.

⁶ Len, *Ber. der Deutsche Physikalische Gesellschaft*, pp. 632-643 (1919).

⁷ Nicholson, *Month. Not. Roy. A. S. Vol. lxxix, (1919)*.

⁸ This incomplete paper was communicated to the Indian Science Congress held at Bombay in January 1919. I find in the January No. of the *Phil. Mag.* that Dr. Silberstein has traversed the same ground and arrived at identical mathematical results, but this paper likewise contains no reduction of the energy-expression to quanta numbers.

⁹ Jacobi, *Vorlesungen über Mathematik*, Article 28-30. Appel, *Traité de Mécanique Rationnelle*, Tome ii. p. 407 et seq.

*Communicated by the Author.

¹ For example, Merton, *Proc. Roy. Soc. Lond.*, vol. xcvi. p. 382; Lenz, *Ber. d. Ph. Gesellschaft*, pp. 632-643 (1919).

² Fabry and Buisson, *Journal de Physique*, pp. 435-445 (1912).

³ Lord Rayleigh, *Phil. Mag.*, vol. xxvii (1889).

⁴ Schönrock, *Ann. d. Physik*, vols. xx & xxii. (1906).

⁵ Saha, *Phys. Rev.*, Dec. 1917.

12. IONIZATION IN THE SOLAR CHROMOSPHERE*

(*Phil. Mag., Sr. VI, 40, 472, 1920*)

§1

It has been known for a long time that the high-level chromosphere is generally distinguished by those lines which are relatively more strengthened in the spark than in the arc, and which Lockyer originally styled as enhanced lines. The following list taken from Mitchell's¹ list of chromospheric lines, along with the respective intensities of the line in the arc and the spark, illustrates the case:—

TABLE I²

Element	Wave-length of the line in A.U.'s.	Chromospheric level reached in Kms.	Intensity.	
			Arc.	Spark.
Calcium	3968 (H)	14000	300	500 L
	3933 (K)		500	1000 L
Strontium	4216	6000	500	500 L
	4078	6000	1000	1000 L
Barium	4994	750	500	1000 L
	4554	1200	1000	1000 L
Scandium	4247	6000	50	1000 L
Titanium	3685.4	6000	8	100
	3741.8	1500	3	10
	3759	6000	10	20 L
	3761	6000	6	10 L
	3900	1600	5	50 L
	3914	2000	5	20 L
	4290	1300	2	10 L
	4294	1200	3	8 L
	4300	1200	3	8 L
	4395	2500	10	10 L
	4444	1600	4	15 L
	4468	1500	4	15 L
	4501	1600	4	15 L
	4563	1200	3	10 L
	4572	1200	5	20 L

This table makes it quite clear that generally only those lines occur in the highest levels which are relatively more strengthened in the spark discharge spectrum. We can add to the above table a list of the high-level iron and other lines, but the conclusion would be the same.

It appears that no satisfactory explanation of this fact, as well as of the extraordinary height reached by these lines, has yet been offered. It is intimately connected with the physical mechanism of the arc and the spark. In this connexion, it is well to recall Lockyer's original hypothesis, which, however, does not seem to have been, at any time,

much in favour with the physicists. According to Lockyer, the passage from the arc to the spark means a great, though localised, increase of temperature, to which mainly the enhancement of the lines was to be ascribed. But, apart from its physical incompleteness, Lockyer's theory launches us amidst great difficulties as far as the interpretation of solar phenomena is concerned. It would lead us to the hypothesis that the outer chromosphere is at a substantially higher temperature than the photosphere, and the lower chromosphere; and that the temperature of the sun increases as we pass radially outwards. This hypothesis is, however, quite untenable and is in flagrant contradiction to all accepted theories of physics.

A much more plausible explanation is that the lines in question are not due to radiations from the normal atom of the element, but from "an ionized atom, *i.e.*, one which has lost an electron." The high-level chromosphere is, according to this view, the seat of very intense ionization. Let us see briefly how this hypothesis has grown up.

Modern theories of atomic structure and radiation leave little doubt that the "enhanced lines" are due to the ionized atom of the element. As a concrete example, let us take the case of the Calcium H, K, and *g* lines. The "H, K" lines are of the enhanced type, while "*g*" is of the normal type. The "H, K" are the leading members of the principal pair-series of the system of double lines of Calcium, while the "*g*" line is the first member of the system of single lines of Calcium. Lorensen and Fowler³ have shown that the series formula of the double lines is of the type

$$\nu = 4N \left[\frac{1}{\{f'(m)\}^2} - \frac{1}{\{\phi'(n)\}^2} \right],$$

while the series formula of the single lines is of the type

$$\nu = N \left[\frac{1}{\{f'(m)\}^2} - \frac{1}{\{\phi'(n)\}^2} \right],$$

where $f(m)$, $\phi(n)$ are functions of the form $m + \alpha$, according to Rydberg, and $m + \alpha + \beta[t(m)]$, according to Ritz, $t(m)$ being a function of m which vanishes with increasing values of m .

In other words, in the series formula of the enhanced lines, the spectroscopic constant is $4N$ instead of the usual Rydberg number N . In the light of Bohr's theory, this is to be understood in the sense that, during the emission of the enhanced lines, the nucleus, and the system of electrons

*Communicated by the Author.

¹Mitchell, *Astrophysical Journal*, vol. xxxviii, p. 424.

²L denotes "enhanced" according to Lockyer.

³Fowler, *Phil. Trans.*, vol. ccciv.

(excluding the vibrating one) taken together behave approximately as a double charge, so that the spectroscopic constant, $=\frac{2\pi^2e^2E^2m}{h^3}$, becomes $4N$, as $E=2e$. This means that if the nuclear charge is n , the total number of electrons is $(n-1)$, and the system has been produced by the removal of one electron from the normal atom.

What has been said of the Calcium lines H and K is also true of the Strontium pair 4216 and 4078, and the Barium pair 4934 and 4554, *i.e.*, they are due to the ionized atom of these elements. The principal lines of the system of single lines of these elements also occur in the flash spectrum, but the following table shows that they reach a much lower level:—

TABLE II.

Element	Lines due to the Ionized Atom	Chromospheric level	Lines due to the Normal Atom	Chromospheric level
Ca	(H) 3968 } (K) 3933 }	14000	(g) 4227	5000
Sr	4216 } 4078 }	6000	4607	350
Ba	4934 } 4554 }	750 } 1200 }	5536	400

N.B.—The lines chosen are the fundamental lines or the first lines of the principal series, having the symbolic formula $\nu=(1.S)-(2.P)$.

No satisfactory series formula is known for the other high-level chromospheric elements, *viz.*, Titanium, Scandium, Iron, and other elements. But the recent remarkable work of Kossel and Sommerfeld⁴ makes it quite clear that the spark-lines of these elements are due to the ionized atom. The spark-lines of alkalis have not been much investigated and lie in the ultraviolet beyond 3000, so that, even if they are present in the high-level chromosphere, we shall have no means of detecting them⁵.

As regards Hydrogen, ionized Hydrogen would mean simply the hydrogen core, and this probably by itself would be incapable of emitting any radiation. But as H_α and H_β lines occur high in the chromosphere, we have to admit that hydrogen probably is not much ionized in the chromosphere.

The case of helium is very interesting. It is well known that the Fraunhofer spectrum does not contain any helium lines, which are obtained only in the flash spectrum. But these lines are all due to normal helium, and the highest level reached by the second line of the so-called principal series is some 8500 kms.⁶, while the better-known D_3 reaches a level of 7500 kms. The lines due to ionized helium are represented by the general series formula

$$\nu=4N\left[\frac{1}{m^2}-\frac{1}{n^2}\right],$$

and the best known of them, in the visible range, are the Rydberg line 4686 and the Pickering system

$$\nu=N\left[\frac{1}{2^2}-\frac{1}{(m+\frac{1}{2})^2}\right]$$

once ascribed to "cosmic hydrogen." Mitchell⁷ states that 4686 occurs in the flash spectrum, and reaches a level of 2000 kms. If the identification be all right, helium would present a seemingly anomalous case, for, whereas other elements are ionized in the upper strata, it is ionized in the lower strata of the chromosphere.

The above sketch embodies, in short, the problems before us. The alkaline earths and the heavier elements are ionized throughout the whole of the solar atmosphere, but the ionization is complete in the chromosphere, which seems to contain no normal atom at all. But hydrogen and helium are probably unionized throughout the whole chromosphere, and in the case of helium we have probably some slight ionization in the lower parts—a rather anomalous case.

The explanation of these problems, and some other associated problems of solar physics, will be attempted in this paper. The method is based upon a recent work of Eggert⁸—"On the State of Dissociation in the Inside of fixed Stars." In this problem, Eggert has shown that by applying Nernst's formula of "Reaction-isobar,"

$$K=\frac{p_M^{\nu_M}p_N^{\nu_N}\dots}{p_A^{\nu_A}p_B^{\nu_B}\dots},$$

to the problems of gaseous equilibrium in the inside of stars, it is possible to substantiate many of the assumptions made by Eddington⁹ in his beautiful theory of the constitution of stars. These assumptions are that in the inside of stars the temperature is of the range of 10^5 to 10^6 degrees and the pressure is about 10^7 Atm., and the atoms are so highly ionized that the mean atomic weight is not much greater than 2. This method is directly applicable to the study of the problems sketched above. The equation of the Reaction-isobar is

$$\log K=\log \frac{p_M^{\nu_M}p_N^{\nu_N}\dots}{p_A^{\nu_A}p_B^{\nu_B}\dots}=-\frac{U}{4.571T}+\frac{\sum \nu C_p}{R} \log T+\sum \nu C, \quad (1)$$

where K =the Reaction-isobar,
 U =heat of dissociation,
 C_p =specific heat at constant pressure,
 C =Nernst's Chemical constant,

and the summation is extended over all the reacting substances. The present case is treated as a sort of chemical reaction, in which we have to substitute ionization for chemical decomposition. The next section shows how U is to be calculated. The equation will be resumed in §3.

⁴Kossel and Sommerfeld, *Ber. d. d. Phys. Gesellschaft*, Jahrgang 21, p. 240.

⁵Kossel and Sommerfeld, *loc. cit.* p. 250.

⁶This line is masked by the strong hydrogen line H_γ .

⁷Mitchell, *loc. cit.* pp. 490-491.

⁸Eggert, *Phys. Zeitschrift*, Dec. 1919.

⁹Eddington, *M. N. R. A. S.* vol. lxxvii. pp. 16 and 596.

§2.

We may regard the ionization of a calcium atom as taking place according to the following scheme, familiar in physical chemistry,



Where Ca is the normal atom of calcium (in the state of vapour), Ca_+ is an atom which has lost one electron, U is the quantity of energy liberated in the process. The quantity considered is 1 gm. atom.

The value of U in the case of alkaline earths, and many other elements, can easily be calculated from the value of the ionization potential of elements as determined by Franck and Hertz, MacLennan¹⁰, and others. Let V=ionization potential. Then, to detach one electron from the atomic system, we must add to each atom an amount of energy equivalent to that acquired by an electron falling through a potential difference V, where V (in volts) is given by the quantum relation,

$$\frac{eV}{300} = h\nu_0, \dots \dots \dots (3)$$

ν_0 being the convergence frequency of the principal series, i.e., (1, s) in Paschen's notation¹¹. If this quantity be multiplied by the Avogadro number N, and expressed in calories, we obtain U.

Thus if V=1 volt, we have

$$U = \frac{eV.N}{J.300} = \frac{9645.10^8}{4.19 \times 10^7} = 2.302.10^4 \text{ calories.}$$

Table III. contains for future use the values of the ionization potentials¹² as far as known, and the calculated

TABLE III.

Element	Ionization Potential	U in Calories
Mg	7.65	$1.761 \cdot 10^5$
Ca	6.12	1.409 "
Sr	5.7	1.313 "
Ba	5.12	1.178 "
Ra	?	?
Na	5.112	1.177×10^5
K	4.318	.994 "
Rb	4.155	.957 "
Cs	3.873	.892 "
Zn	9.4	2.164×10^5
Cd	9	2.072 "
Hg	10.45	2.406 "

value of U. Here I wish to remark that an element may have more than one ionization potential, depending upon the successive transfer of the outer electrons one by one to

infinity, or the simultaneous existence of two more constitutions of the normal atom (e.g. helium and parhelium). The ionization potential given in the table corresponds to the case when only one electron is transferred to infinity leaving an excess of unit positive charge in the atom. We have made it clear in the introduction that the high-level alkaline earth-lines are due to the atoms with one plus charge in excess.

The cases of hydrogen and helium will be taken up later on.

§3. Equation of the Reaction-isobar for Ionization.

As mentioned in the introduction, the equation of gaseous equilibrium proceeds according to the equation,

$$\log K = -\frac{U}{4.571T} + \frac{\sum \nu C_p}{R} \log T + \sum \nu C, \dots \dots (1)$$

where the reaction proceeds according to the scheme,

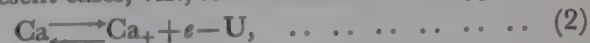


and K is the "Reaction-isobar",

$$\frac{p_m^{\nu_m} p_n^{\nu_n} \dots}{p_a^{\nu_a} p_b^{\nu_b} \dots}$$

$p_m^{\nu_m}, p_n^{\nu_n} \dots$ being the partial pressures of the reacting substances—M, N, etc.

In the present cases, viz., for a reaction of the type,



we have

$$\sum \nu C_p = (C_p)_{\text{Ca}_+} + (C_p)_e - (C_p)_{\text{Ca}}.$$

We can take

$$(C_p)_{\text{Ca}} = (C_p)_{\text{Ca}_+},$$

and $(C_p)_e = \frac{5}{2}R$, the electron being supposed to behave like a monatomic gas.

Eggert calculates the chemical constant from the Sackur-Tetrode-Stern relation,

$$C = \log \frac{(2\pi M)^{\frac{1}{2}} k^{\frac{3}{2}}}{h^3 N^{\frac{1}{2}}} = -1.6 + \frac{5}{2} \log M, \dots \dots \dots (4)$$

where M=molecular weight, the pressure being expressed in atmospheres.

Now C has the same value for Ca and Ca_+ . For the electron $M = 5.5 \times 10^{-6}$, and $C = -6.5$.

We have thus

$$\sum \nu C = -6.5 \dots \dots \dots (5)$$

To calculate the "Reaction-isobar" K, let us assume that P is the total pressure, and a fraction x of the Ca-atoms is ionized.

Then we have

$$\log K = \log \frac{x^2}{1-x^2} P = -\frac{U}{4.571T} + 2.5 \log T - 6.5. \dots (1')$$

This is the equation of the "reaction-isobar" which is throughout employed for calculating the "electron-affinity" of the ionized atom.

¹⁰MacLennan, 'Proceedings of the Physical Society of London,' Dec. 1918.

¹¹Paschen uses the symbol (1.5, s), but following Sommerfeld (*loc. cit.* p. 243), I have taken off .5 and used (1, s).

¹²MacLennan, *loc. cit.* p. 18.

Ionization of Calcium, Barium, and Strontium.

With the aid of formula (1), the degree of ionization for any element, under any temperature and pressure, can be calculated when the ionization potential is known. As a concrete example, we may begin with Calcium, Strontium, and Barium.

A glance at equation (1') shows that pressure has a very great influence on the degree of ionization, which does not seem to have been anticipated. This is due to the occurrence of P in the first power in the expression for the "Reaction-isobar." A reduction in the value P is attended with greatly enhanced ionization. This will become apparent from an inspection of the following tables, which show the ionization of Calcium, Strontium, and Barium under varying conditions of pressure and temperature.

TABLE IV.

Ionization of Calcium (in per cents.).

 $U = 6.12 \text{ volts} = 1.40.10^5 \text{ calories approximately.}$

Pressure in atmospheres—Temperature on the Absolute Scale.

Pressure Temp.	10.	1.	10^{-1} .	10^{-2} .	10^{-3} .	10^{-4} .	10^{-5} .	10^{-6} .
2000°					5.10^{-4}	$1.4.10^{-3}$		
2500					2.10^{-3}	7.10^{-2}		
3000					3.10^{-1}	1	9	
4000				2.8	9	26	93	
5000			2	6	20	55	90	
6000	2	8	26	64	93	99		
7000	7	23	68	91	99			
7500	11	34	75	96.5				
8000	16	46	84	98.5				
9000	29	70	95					
10000	46	85	98.5					
11000	63	93						
12000	76	96.5						
13000	84	98.5						
14000	90							

TABLE V.

Ionization of Strontium (in per cents.).

 $U = 1.3 \times 10^5 \text{ calories.}$

Pressure Temp.	10.	1.	10^{-1} .	10^{-2} .	10^{-3} .	10^{-4} .	10^{-5} .	10^{-6} .
2000°					$1.2.10^{-3}$	4.10^{-3}		
2500					6.10^{-3}	2.10^{-1}		
3000			7.10^{-3}	2.10^{-2}	7.10^{-2}	2.5		
4000			1.6	5	15	45	98.5	
5000	1	3.2	11	32	73	96		
6000	4	13	37	78	97			
7000	10	32	73	96				
7500	15	45	84	98.5				
8000	22	58	91	99				
9000	38	79	97.5					
10000	56	90	98.5					
11000	71	95						
12000	82	97.5						
13000	89	98.5						
14000	93							
15000	96							

TABLE VI.

Ionization of Barium (in per cents.).

 $U = 1.2.10^5 \text{ calories approximately.}$

Pressure Temp.	10.	1.	10^{-1} .	10^{-2} .	10^{-3} .	10^{-4} .	10^{-5} .	10^{-6} .
2000°					6.10^{-3}	2.10^{-2}	2.10^{-1}	
2500					$1.8.10^{-1}$	7.10^{-1}	6	
3000					1.6	5	46	
4000		1	3	9	28	68	99	
5000	1.7	5.5	17	48	86	98		
6000	6.2	19	52	88	99			
7000	15	43	83	98				
7500	22	57	91					
8000	30	70	94					
9000	47	85						
10000	65	93						
11000	97							
12000	99							

Complete
Ionization.

We are not aware how the temperature and the pressure (partial pressure for a particular element) vary with height in the solar atmosphere. According to F. Biscoe¹³, the temperature of the photosphere is about 7500°K., while the pressure in the reversing layer varies, according to different investigators, from 10 to 1 atmospheres. If we suppose that the variation in temperature is entirely caused by radiation, the temperature of the upper layers should tend to the limit $\frac{7500}{2^{\frac{1}{2}}}$ ¹⁴ or a little more than 6000°K.

The partial pressure may be supposed to vary from 10 atmospheres in the reversing layer to 10^{-12} atmosphere in the outermost layers.

An examination of Tables IV., V., VI. shows that, under the above-mentioned assumptions, about 34 per cent. of the Ca-atoms are ionized on the photosphere. When the pressure falls to 10^{-4} atmosphere, almost all the atoms get ionized, so that up to this point in the solar atmosphere, we shall get combined emission of the H, K, and the g -line, but above this point, we shall have only the H, K lines. This is in very good agreement with observed facts.

In the case of strontium and barium, owing to their comparatively low ionization potential, ionization at 6000° is practically complete at 10^{-3} atmosphere, and the heights shown by the lines of the unionized atoms of these elements are still lower. Compare the Tables IV., V., VI.

The results of the flash-spectrum observations are thus seen to be very satisfactorily accounted for on the basis of our theory.

Laboratory experiments also, as far as they go, are in qualitative agreement with our theory. It is well known that in the flame, the flames due to the ionized atom either do not occur at all, or even if they do occur they are extremely faint compared with the lines of the unionized atom.

¹³ F. Biscoe, *The Astrophysical Journal*, vol. xlv. p. 355.¹⁴ Schwarzschild, *Gott. Nachrichten*, p. 41 (1906).

As the temperature is increased, the "enhanced lines" begin to strengthen, until at the temperature of the arc they are comparable in intensity to the lines of the normal atom.

We give below the results of King¹⁶ on the relative intensity of the "enhanced" and ordinary lines of the alkaline earths in vacuum-tube furnaces at varying temperatures. Unfortunately, the pressure, which is a vital point, is not mentioned. The last line shows the percentage of the ionized atoms under a pressure of 10^{-4} atmosphere, or .1 mm. of mercury.

The tables show that an increase of temperature causes an increase of ionization and the proportion of emission centres of the enhanced lines. The increasing intensities of the double lines are mainly to be ascribed to this fact. These become comparable in intensity to the principal lines of the normal atom only when the degree of ionization is rather large (comp. the figures at 4000°). Comparing the relative intensities of the corresponding lines of the calcium and barium group, we find that for the same temperature the enhanced lines of barium are relatively stronger than the calcium lines; and this, according to our theory, is due to the comparatively lower ionization potential of barium.

The objection may be raised whether the proportion of ionized atoms at low temperatures, as given by the theory, is not rather too low. The tables show that at 2000° K., only 1 in 10^6 calcium atoms is ionized. Is this small number of ionized atoms capable of affecting the photographic plate by the emission of the H and the K lines?

No definite answer can be given to this point. We may, however, point out that, according to Ladenburg and Loria¹⁶, when a hydrogen vacuum tube at a pressure of a few mms. of mercury is excited by a spark, only 1 atom in 50,000 is found to be radiant, *i.e.*, capable of emitting H α and H β . A very low proportion of radiant centres may therefore affect the photographic plate. It should also be remembered that at low temperatures the principal line of the normal atom is not only relatively more intense, but very broad and diffuse, when the enhanced lines are extremely narrow in addition to being faint.

A reduction in pressure will cause the relative intensity of the H-K line to increase, but not the absolute intensity, because the total available number of radiant particles will now decrease. I am not aware whether there is any laboratory experiment for testing this point.

§ 4. Hydrogen in the Sun.

It has been mentioned in the introduction that hydrogen is not appreciably ionized at even the highest levels of the solar chromosphere. We should add to this the fact that hydrogen exists in the Sun only in the atomic state, for, if there were molecular hydrogen in the Sun, we could have detected some at least of the lines of the secondary spectrum. But this is not the case; hydrogen enters into chemical combination with calcium and magnesium in the sun-spot, but does not probably form molecules of its own.

TABLE VII.

Element.	Temp.					Photosphere	Chromosphere.
	Actual Approx. Line.	1923 2000	2273 2500	2623 3000	Arc. 4000	7500	6000
		Intensity.					
Ca	4227 (g)	300	500	1000	500	20	25
Ca+	3968 (H)	18	25	50	350	700	80
	3933 (K)	20	30	60	400	1000	100
Proportion of ionized atoms in per cents.		$1.4 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	1	26	75 ($P=10^{-1}$)	93 ($P=10^{-3}$)
Sr...	4607	300	400	600	600	1	2
Sr +	4216 }	6	15	30	400	5	40
	4078 }	12	25	40	400	8	40
Proportion of Sr+ in per cents.		$4 \cdot 10^{-3}$	$2 \cdot 10^{-1}$	2.5	45	84 ($P=10^{-1}$)	97 ($P=10^{-3}$)
Ba	5536	400	500	1000	1000	2	1
	4934 }	50	60	70	700	7	12
	4554 }	70	80	100	1000	8	20
Proportion of Ba+ in per cents.		$2 \cdot 10^{-3}$	$7 \cdot 10^{-1}$	5	68	91 ($P=10^{-1}$)	98 ($P=10^{-3}$)

N.B.—The intensity scale under the headings photosphere and chromosphere is different from the scale in King's furnace spectra.

¹⁶ King, 'The Astrophysical Journal,' vol. xlviii. p. 13.

¹⁶ Ladenburg and Loria, *Ber. d. D. Phys. Gesellschaft*, 1908.

The distinction between He and the so-called parhelium is taken as one of relative configuration of the steady orbits

of the two electrons²⁰. V_2 may be identified with 20.5 volts, V_1 with 25 volts, and V_3 with $4.13 \cdot 6 = 54.6$ volts²¹.

Taking $V_2 = 20.5$ volts, $U = 4.8 \times 10^5$ calories approximately, we have the following table for the first step ionization of parhelium. If the ionization voltage be taken $= 25$ volts, the degree of dissociation will become still less:—

TABLE IX.
Ionization of Helium (in per cents.)
 $U = 4.8 \cdot 10^5$ calories (approximately).

Pressure Temp.	1.	10^{-1} .	10^{-2} .	10^{-3} .	10^{-4} .	10^{-5} .
6000°	5.10^{-6}	$1.7 \cdot 10^{-6}$	5.10^{-5}	$1.7 \cdot 10^{-4}$	5.10^{-3}	5.10^{-2}
7000	1.10^{-4}	$3.6 \cdot 10^{-4}$	1.10^{-3}	$3.6 \cdot 10^{-3}$	1.10^{-2}	1.10^{-1}
7500	4.10^{-4}	$1.2 \cdot 10^{-3}$	4.10^{-3}	$1.2 \cdot 10^{-2}$		
8000	$1.2 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$	$3.7 \cdot 10^{-2}$	$1.2 \cdot 10^{-1}$	$3.7 \cdot 10^{-1}$
9000	7.10^{-3}	$2.3 \cdot 10^{-2}$	7.10^{-2}	$2.3 \cdot 10^{-1}$	7.10^{-1}	7
10000	3.10^{-2}	1.10^{-1}	3.10^{-1}	1	3	31
11000	1.10^{-1}	$3.4 \cdot 10^{-1}$	1	3.4	11	72
12000	3.10^{-1}	1	3	10	28	93
13000	7.10^{-1}	2	7	22	58	
14000	1.5	4	15	43	83	
15000	3	10	28	68	94	
16000	6	17	47	85		

The table shows clearly the ionization of helium is too slight under the conditions in the solar atmosphere, both in the reversing layer ($T = 7500^\circ$, pressure = 1 atm.), as well as in the high-level chromosphere ($T = 6000^\circ$, $p = 10^{-8}$ atmos.). But somewhere between the two ($T = 7000^\circ$, $p = 10^{-3}$ atm.), there may be some slight ionization (1 in 10,000) which may account for the occurrence of the line of ionized helium $\lambda = 4686$, which has been detected by Mitchell. The calculations are, of course, of the roughest nature.

The investigation also incidentally shows that the Pickering lines $\nu = N \left[\frac{1}{2^2} - \frac{1}{(m + \frac{1}{2})^2} \right]$ and the Rydberg line 4686 can occur as absorption-lines only in stars having the highest temperature, exceeding $16,000^\circ \text{K}$. This seems to be independently borne out by the investigations of Eddington and Russell.

The application of the method and the results obtained in the present paper to the problems of temperature radiation of elements and of the different spectral types of stars

²⁰See a paper by Lande, *Ber. d. D. Phys. Gesellschaft*, 1919.

²¹It is not possible to deduce V from the quantum relation $eV = h(1, s)$, for the fundamental term $(1, s)$ is unknown both for helium and parhelium. What are generally called the principal series of helium are really the series $\nu = (2, s) - (m, p)$ (the leading lines being 10380, for He and 20587 for parhelium).

naturally suggest themselves, and will be taken up in a future communication.

Summary

1. In the present paper it has been shown from a discussion of the high-level chromospheric spectrum that this region is chiefly composed of ionized atoms of Calcium, Barium, Strontium, Scandium, Titanium, and Iron. In the lower layers both ionized and neutral atoms occur.

2. An attempt has been made to account for these facts from the standpoint of Nernst's theorem of the "Reaction-isobar," by assuming that the ionization is a sort of reversible chemical process taking place according to the equation $\text{Ca} \rightleftharpoons \text{Ca}_+ + e - U$. The energy of ionization U can be calculated from the ionization-potential of elements as determined by Franck and Hertz, and MacLennan. For determining Nernst's chemical constant and the specific heat, the electron has been assumed to be a monatomic gas

having the atomic weight of $\frac{1}{1836}$.

3. The equation shows the great influence of pressure on the relative degree of ionization attained. The almost complete ionization of Ca, Sr, and Ba atoms in the high-level chromosphere is due to the low pressure in these regions. The calculated values are in very good accord with observational data and the laboratory experiments of King.

4. Hydrogen has been shown to be completely dissociated into atoms at all points in the solar atmosphere.

5. It has also been shown that the greater the ionization potential of an element, the more difficult ionization will be for that element under a given thermal stimulus. Calculations have been made in the case of hydrogen ($V = 13.6$ volts) and helium ($V = 20.5$ volts), which show that these elements cannot get ionized anywhere in the Sun to an appreciable extent. Helium can have appreciable ionization only in stars having the highest temperature ($> 16,000^\circ \text{K}$), which only are therefore capable of showing the Rydberg line 4686 and the Pickering lines $\nu = N \left[\frac{1}{2^2} - \frac{1}{(m + \frac{1}{2})^2} \right]$.

In conclusion, I beg to record my best thanks to my students for their valuable help in the calculations, and to my friend Dr. J. C. Ghosh for revising the proofs.

Calcutta, India.

March 4, 1920.

13. ELEMENTS IN THE SUN* (PAPER B)†

(*Phil. Mag., Sr. VI*, 40, 809, 1920)

It is a matter of common knowledge that the continuous spectrum from the photosphere of the sun is crossed by a number of dark lines, which are called Fraunhofer lines in honour of their eminent discoverer. The correct interpretation of these lines was given by Kirchhoff in 1859, who showed that most of the principal lines can be attributed to the absorption of light of proper frequency by the cooler layers of the vapour lying above the photosphere. Since this epoch-making discovery, it has become a part of the routine work of astrophysicists to catalogue and properly measure the wave-length of these lines, and identify them with the emission lines of elements obtained in the laboratory.

The most extensive mapping of the Fraunhofer spectrum is due to Rowland, who counted and catalogued about 20,000 lines, but of these only 6000 have been identified with the lines of known elements. By this means, the presence of thirty-six elements has been definitely established in the sun, with doubtful indications of eight or more. The following are the elements of the existence of which in the sun no evidence yet been obtained¹ in:—

(a) Rubidium, Caesium, Nitrogen, Phosphorous, Boron, Antimony, Bismuth, Arsenic, Sulphur, Selenium, Thallium, Praseodymium.

Doubtful indications have been obtained of the existence of the following elements:—

(b) Radium², elements of the inert group with exception of Helium, which is obtained in the flash spectrum, Osmium, Iridium, Platinum, Ruthenium, Tantalum, Thorium, Tungsten, Uranium.

The following elements are represented by very faint lines in the Fraunhofer spectrum:—

(c) Potassium, Copper and Silver; Cadmium and Zinc; Tin and Lead; and Germanium.

(d) Chlorine, Bromine, Iodine, Fluorine, Tellurium, and many other elements have not been investigated at all.

No satisfactory explanation has yet been offered of the complete non-existence of the lines of elements mentioned in group (a) or (b), or of the faint occurrence of the lines

of elements mentioned in group (c). Similarly, it has not yet been made clear why certain elements like Ca, Fe, V, Ti are so unusually prominent in the solar spectrum. They are represented not only by the absorption lines of the neutral atom, but also by the absorption lines of the ionized atom (enhanced lines).

It is sometimes assumed that these phenomena are due to the chemical composition of the sun—in other words, the elements of which no lines are found either in the Fraunhofer or the flash spectrum are totally absent from the sun. But this view is most unsatisfactory, and can only be regarded as a stop-gap. There is, *à priori*, no reason why, in the sun, certain elements should be preferred to the exclusion of others. On the contrary, it seems natural to infer that the sun is composed of the same elements as the earth, and contains all the 92 elements known to the chemists on the earth.

It therefore becomes increasingly necessary to investigate why certain elements should entirely fail to be recorded on the Fraunhofer or the flash spectrum. It may be supposed that certain elements fail to be recorded because, on account of their heavy atomic weight, they are practically confined to the photosphere. But it is not merely a question of atomic weight, for in the list of missing elements we find light elements like boron and nitrogen side by side with a heavy element like thallium.

The view which is urged in the present paper is that the varying records of different elements in the Fraunhofer spectrum may be regarded as arising from the varying response of these elements with regard to the stimulus existing in the sun. The stimulus existing in the sun is the same for all elements, *viz.*, that arising from a temperature of about 7500°K., but owing to a different internal structure, elements will respond in a varying degree to this stimulus. The manner in which we can quantitatively estimate the effect of the stimulus has been sketched in papers A and C.³ In paper A, the effect of the stimulus on the alkaline earths Ca, Sr, and Ba was estimated. It was shown that while on the photosphere 30, 40 and 57 per cent. of the atoms are respectively ionized, the percentage of ionization increases with height and becomes practically complete for Ca at a pressure of 10^{-6} atm., for Sr at a pressure of

*Much of the introduction is taken, *mutatis mutandis*, from Fowler's report on the subject; vide 'Journal of the British Astronomical Society', May 1918.

†Communicated by the Author.

¹Pringsheim, *Physik der sonne*, p. 116.

²For the controversy regarding the existence of Radium, and the members of the inert group in the flash-spectrum, see 'Observatory', vol. xxxv. pp. 297, 357 and 402.

³Paper A—"Ionization in the Solar Chromosphere", *Phil. Mag.* Oct 1920; Paper C—"On the Temperature Radiation of Gases" (To appear shortly).

10^{-3} , and for Ba at a pressure of 10^{-2} atm. In this connection it may prove interesting to compare the results with the following remarks of Fowler:

"We find further, that while many of the metals are represented by both arc and enhanced lines, there are some which are identified only, or mainly, by their enhanced lines alone. Thus, although Ca shows both classes of lines strongly, Sr and Ba practically show enhanced lines alone".

Fowler ascribes the different behaviour of Ca on the one hand, and Sr and Ba on the other hand, to their differences in atomic weight, but according to the view presented in Paper A, this is mainly due to the varying values of the *ionization potential*. The author's belief is that in the sun and the stars, the attraction due to gravity is largely compensated by selective radiation pressure, and atomic weight is of much less consequence than can be supposed.

The method sketched in paper A has been extended to the alkali metals, and a few other elements. It will be seen that the theory accounts in a most gratifying manner for the varying behaviour of sodium lines in the Fraunhofer spectrum, and its intensification in the sun-spot spectrum, for the faint occurrence of the potassium lines, and for the complete absence of the lines of Cs, and Rb, and for the varying behaviour of the lines of Mg and Mg^+ , though, on this last point, the results are not so satisfactory. There is very little doubt that if proper data be available, the method can be extended to the explanation of all the details of the Fraunhofer spectrum.

For the explanation of the method, the reader is referred to Section 2 and 3 of paper A. The temperature of the photosphere has been taken to be $7500^\circ K.$, the pressure 1 to 10^{-1} atm., while for the high-level chromosphere a temperature of $6000^\circ K.$, has been used.

1. THE ALKALI ELEMENTS IN THE SUN

(a) Sodium

The following table shows the ionization of sodium in percents. under varying conditions of temperature and pressure:

Ionization Potential = 5.12 volts = 1.17×10^6 calories

Pressure Temp.	1.	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
5000	6	19	53	89	98.5	
6000	21	56	90	98.5		
7000	46	85	98			
7500	60	72	99			
8000	72	96				Complete Ionization.
9000	87	98.5				
10000	97					

The table shows that under the solar conditions, 60 per cent of sodium atoms are ionized in the photosphere, and ionization is practically complete at a level where the pressure falls to 10^{-3} atm. The result is in very good agreement with observational facts, for according to Mitchell the D_1 and D_2 lines reach a level of only 1200 kms. Over this height, only ionized Na-atoms are present, the chief emission lines of which lie, according to Goldstein⁴, in the remote ultra-violet, and so escape detection.

Taking the temperature of the spot = $5000^\circ K.$,⁵ we see from the tables that only 6 to 19 per cent of the atoms are ionized. So over the spot, there is a great increase in the proportion of unionized Na-atoms, and we should expect a much stronger absorption of the D_1 and D_2 lines. The following table (taken from Kayser's *Handbuch der Spektroskopie*, vol. vi. p. 114) shows that this is actually the case:

Line	Series-Description	Intensity in the Sun	Intensity in Sun-spot spectrum
D_1 —5896.15	(1,s)—(2, p_2)	20	60
D_2 —5890.19	(1,s)—(2, p_1)	30	90
5682.90	(2, p_2)—(3,d)	5	12
5688.26	(2, p_1)—(3,d)	6	12
6154.44	(2, p_2)—(3,s)	2	8
6161.95	(2, p_1)—(3,s)	3	9

(b) Potassium

The identification of Potassium is rather doubtful. Rowland has identified only two faint Fraunhofer lines $\lambda=4047.36$, 4044.29 , with the emission lines (1, s)—(3, p_1), (1, s)—(3, p_2) of potassium. The following table shows that owing to the low value of the ionization potential, potassium is highly ionized throughout the whole of the solar atmosphere.

Ionization of Potassium

Ionization Potential = 4.318 volts = 1.00×10^6 calories.

Pressure Temp.	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
3000			2.5	9	28	66
4000	3	11	32	72	97	
5000	15	44	83	98		
6000	41	81	97.5			
7000	70	95				Complete Ionization.
7500	81	98				
8000	87	99				
9000	94					
10000	98					

⁴ Goldstein, *Ann. d. Physik*, vol. xxvii. pp. 773-796; Schillinger, *Wien. Ber.* p. 608 (1919); Nelthorpe, *Astrophysical Journal*, Jan. 1915.

⁵ Emden, *Gas-kugeln*, p. 443. See also numerous papers on the spectra of sun-spots by Fowler, Hale, and others.

The identification of potassium is to be carried by the lines $(1, s)-(3, p_1)$, $(1, s)-(3, p_2)$ which under all circumstances are likely to be much less intense than the leading pair $(1, s)-(2, p_1)$, $(1, s)-(2, p_2)$ which lie in the infra red, $\lambda=7665.3$, 7699.3 . This fact, combined with the high proportion of ionization, tends to make the identification rather difficult. The lines of the ionized atom lie in the ultra-violet and so escape detection (Goldstein, *Astro. Journal*, xxvii. pp. 25-34 (1908) and *Ann. d. Phys.* loc. cit).

Over the spots the potassium lines ought to be strengthened, but no observation seems to have been made on this point.

(c) Rubidium

As has been mentioned in the introduction, no lines of Rubidium have been identified in the Fraunhofer spectrum of the sun, though in the usual flame and arc spectrum there are many strong lines within the available range.

The following table shows the ionization of rubidium. It will be apparent from the tables that in the sun rubidium is completely ionized. Consequently, even if it be present, we shall get the lines due to the ionized atoms only, which according to Goldstein⁶, lie in the ultra-violet. The spot spectrum should show some faint rubidium lines. But no observation seems to have been made on this point.

Ionization Potential $U = .96 \times 10^5$ calories = 4.16 volts.

Pressure Temp.	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
2000						1
2500				2	6	20
3000		1	4	13	37	78
4000	4	17	39	80	98	
5000	19	51	87			
6000	46	85	98			
7000	75	97				
7500	84	98				
8000	90					
9000	96					
10000	99					

(d) Caesium

No Caesium lines have been identified in the Fraunhofer spectrum. The case is identical with that of rubidium, only in a more marked degree. A table of the ionization

of caesium is appended below:

$U = 3.88$ volts = $.90 \times 10^6$ calories.

Pressure Temp.	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
2000					3	8
2500			1	4	11	34
3000		1	4	12	35	75
4000	7	20	53	89	98.5	
5000	25	62	92			
6000	56	90				
7000	81	97.5				
7500	88	99				
8000	92					
9000	98					

Complete
Ionization.

Oxygen

The presence of oxygen in the sun was a matter of great controversy until a few years ago. The well-known bands A, B, α were shown by Jansen⁷ to be of telluric origin—i.e., caused by the absorption of the solar light by the molecular oxygen of our own atmosphere. But Runge and Paschen identified the weak Fraunhofer triplet, $\lambda=7772.20$, 7774.43 and 7775.62 , lying in the extreme red, with the three emission lines of oxygen, having the series formula

$$(2, s)-(m, p_1), (2, s)-(m, p_2), (2, s)-(m, p_3).$$

In the sun, therefore, oxygen exists in the atomic state.

The heat of decomposition of the oxygen molecule is not yet known with certainty. From Langmuir's⁸ observation that at 2400°K . and 10^{-1} atmospheric pressure oxygen is completely dissociated, I have calculated provisionally the heat of decomposition to be less than 50,000 calories, which is less than the corresponding value for hydrogen (84,000 cal.). Since the equation of chemical equilibrium is almost the same in both cases⁹, it follows without any calculation that oxygen should be completely decomposed into atoms in the sun. The ionization potential of oxygen is probably large, and no lines due to ionized oxygen seem to occur in the sun.

The lines of O^+ and O^{++} have been qualitatively studied by Lunt, Fowler¹⁰, and Brooksbank, but no series-formulae have yet been obtained for these lines. But Fowler's identification of certain of these lines in the Bo-class of stars and in Wolf-Rayet stars respectively seem to indicate that the first step ionization of oxygen is reached at an approximate temperature of $20,000^\circ\text{K}$. and second step ionization at probably not less than $30,000^\circ\text{K}$.

⁷ Pringsheim, *Physik der Sonne*, p. 119 et seq.

⁸ Langmuir, *Journ. Chem. Soc.*, vol. xxxiv. pp. 864, 1030 (1912)

⁹ Vide Hydrogen in the Sun, Paper A, p. 483.

¹⁰ Fowler and Brooksbank, *Month. Not. Roy. Astr. Soc.*, April 1917.

Magnesium

The wave-lengths of the strongest lines of the emission spectrum of Mg. viz. lines $(1, s) - (2, p)$, $(1, s) - (2, p_2)$, lie beyond the range of atmospheric absorption, so that we have to fall upon the next strongest lines, the triplet $(2, p) - (3, d_i)$, $i=1, 2, 3$, $\lambda = 3838.34, 3832.46, 3825.51$, which are very prominent in the flash spectrum, and reach, according to Mitchell, a level of about 7000°km . The height reached by the line $(1, s) - (2, p)$, $\lambda = 2852$, if it were available for observation, would probably be somewhat higher, say about 9000°km . The brief is strengthened from an examination of the table of ionization given below.

Ionization of Magnesium.
Ionization Potential = 7.65 volts = 1.76×10^5 calories.

Pressure Temp.	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
4000		$2 \cdot 10^{-2}$	1	2	9
5000	$5 \cdot 10^{-2}$	1	4	11	32
6000	2	6	18	50	87
7000	6	20	54	89	98
7500	11	32	73	96	
8000	17	47	85	98	
9000	34	75	96		
10000	56	90	98		
11000	75	96			
12000	86	98			
13000	93	99			
14000	96				
15000	98				
16000	99				

Complete
Ionization.

As the ionization potential of magnesium is rather high, it is ionised to a lesser extent than the other alkaline earths. Total ionization is reached at a pressure of about 10^{-6} to 10^{-7} atm. in the chromosphere. This is in excellent accord with observational results.

The lines of ionized magnesium have been studied by Fowler. The lines which should theoretically¹¹ turn out to be strongest, all lie in the ultra-violet, as the following table shows—

$(1, s) - (2, p_1)$	2795.5 Å.U.
$- (2, p_2)$	2802.7
$(2, p_1) - (3, d_1)$	2798.1
$(2, p_2) - (3, d_2)$	2790
$(3, d_1) - (4, f)$	4481,

¹¹Fowler, Phil. Trans. vol. ccxiv. The intensity given for 4481 is relatively much greater than the intensity of the $(1, s) - (2, p)$ lines.

so that the only line available for observation is the leading member of the Bergmann series λ -4481 Å.U. According to observation, this reaches a level of 450 km. only.

According to the considerations presented in paper C, lines of this description under all circumstances require not only a higher stimulus, but also a high density of the radiant particles. Though the upper layers of the chromosphere favour relatively stronger ionization, yet the density is so small that such lines fail to be recorded. They are recorded only from the lower regions where the density is sufficiently great, and the stimulus is not much weakened.

Nitrogen in the Sun

The emission spectrum of Nitrogen is a rather difficult matter to deal with. Under the stimulus in which most of the other elements can be made to emit their characteristic line spectrum or even their enhanced lines, nitrogen gives only several classes of band or molecular spectra. The line spectra seem to require a very great stimulus for their production. But the existing knowledge on the subject is too meagre to allow the discussion of the line emission of atomic nitrogen from the present standpoint. According to a recent paper, the ionization potential of N is 17-18 volts, but this must be made up of the energy of dissociation of the molecule plus the energy of ionization of the atom.

If the so-called cyanogen band having its head at $\lambda = 3883^{12}$ be really due to molecular nitrogen, the conclusion follows that in the sun nitrogen occurs in the molecular state. There may be a fair proportion of atomic nitrogen, but the stimulus is not sufficiently strong to make it emit the lines we are familiar with. All these characteristics are in very good accord with the chemical inertness of nitrogen, which is again due to the high value of the heat of dissociation of the N_2 molecule. The fact is only qualitatively known. According to Langmuir¹³, less than 5 per cent of nitrogen is dissociated at 3500°K . and at atmospheric pressure. From this we may calculate the heat of dissociation in the following manner. The reaction takes place according to the scheme



and if x be the fraction dissociated, P the partial pressure, we have

$$\log \frac{x^2}{1-x^2} P = - \frac{U}{2.3 RT} + \frac{3}{2} \log T + \Sigma C.$$

$$\text{Now } \Sigma C = 2 C_N - C_{\text{N}_2}.$$

According to the Tetrode-Sackur formula,

$$C_N = -1.6 + \frac{3}{2} \log M = .119,$$

¹²This is the opinion of Runge and Grotian (*Phys. Zeits.* vol. xv. 1914). Fowler, on the contrary, believes that the band is due to CN (cyanogen). See also Barratt, Proc. Roy. Soc. Lond. vol. xcvi.

¹³Langmuir, *Journal of the American Chem. Soc.*, vol xxxiv. p. 860 (1919).

and $C_{N_2} = -0.05$.¹⁴

Taking $x=0.03$ in Langmuir's experiment, we can calculate U from the above formula; we obtain

$$U = 1.50 \times 10^5 \text{ calories, in round numbers.}$$

Taking $T=7000^\circ\text{C}$., we can now calculate the value of $\log \frac{x^2}{1-x^2} P$. This becomes 1.390. If $P=1$ atm., almost 98 per cent of the nitrogen ought to be completely broken up into atoms. For $P=10$ atms., the proportion is 83 per cent.

Thus the calculation does not seem to favour the suggestion that a certain percentage of nitrogen occurs in the sun in the molecular state. But the data used for calculation are of the roughest nature, and nothing definitely can be said until better data are available.

Helium

It is well known that none of the Helium lines occur in the Fraunhofer spectrum, though occasional reversals of the D_3 have been observed in the spectra of the penumbra of sun-spots¹⁵. But in the flash spectrum, helium lines are very prominent, the D_3 reaching a height of 7500 km. in the chromosphere. These facts may be explained in the following manner:

The lines by means of which helium is detected belong to the series-combination $(2, p) - (m, d)$, or $(2, s) - (m, p)$. These lines cannot be absorbed by the ordinary He-atoms, which possess $(1, s)$ orbits, but by such atoms as possess the $(2, p)$ or $(2, s)$ orbits. These orbits can only be produced under very great stimulus. It is known from the 'Harvard Annals' (vol. xxviii. 91) that the absorption lines of helium disappear below stars of the A_0 class. Hence a temperature of about $11,000^\circ\text{K}$. (temperature of the A_0 class) is required for producing a sufficient number of He-atoms with $(2, p)$ orbits, when the pressure is one atmosphere. These conditions are not attained on the photospheric level; but at great heights, owing to diminished concentration, not only (m, p) but also (m, d) orbits are produced. As these absorbing atoms occur only at large heights in regions of low concentration, they are not in sufficient number to produce a weakening of the corresponding regions of the continuous spectrum by absorption.

The occasional reversals of He-lines in the penumbra of sun-spots seem to be an effect of diminished concentration without a corresponding loss in temperature. The temperature of the penumbra is intermediate between those of the spot and the undisturbed photosphere, and may be supposed to lie between 6500°K and 7000°K . We have no direct observational result which can give us some idea of the pressure, but Evershed¹⁶ has found

that gases are flowing through the penumbra radially outwards, parallel to the surface of the sun, with velocities ranging from rather small values to about three or four kilometers per second. As the mass-motion of a quantity of gas is always attended with a fall in pressure, the penumbral regions certainly possess lower pressure than the undisturbed photosphere. The physical conditions in the penumbra are therefore favourable to the production of a larger percentage of He-atoms with the $(2, p)$ orbits. Probably this accounts for the occasional weak reversal of He-lines over the penumbra.

The Flash Spectrum

From paper A and the foregoing part of the present paper, it will be seen that Fraunhofer spectrum can mainly be regarded as function of a single physical condition, viz., the temperature. The flash spectrum is, on the other-hand, a function of temperature and concentration, a low concentration favouring a greater percentage of ionization and consequently a *relative* intensification of the enhanced lines. Special attention is called to the word "relative" when terrestrial sources of limited extent are considered, for though the percentage of ionized atoms becomes greater, the absolute number of particles becomes less, and hence all lines, as a rule, become fainter. But the lines of neutral atoms would become much fainter than the enhanced lines.

All this was substantially stated in paper A, but at the time of writing this paper I was acquainted with no experimental work which could be cited in support of the view. I have since come across some works which support my case. The following is an experimental work by Loving on the comparative intensities of Ca and Mg lines in ordinary arc and vacuum arc. (Astrophysical Journal, vol. xxii, p. 300, 1905). Fowler also noted that the enhanced lines of Mg, Zn, and Cd are greatly intensified in a vacuum arc (Fowler and Payn, Proc. Roy. Soc. lxxii. 1903).

Element	Open arc	Vacuum arc	Relative weakening	Spark	Chromosphere
K-3934	500	25	$\frac{1}{20}$	1000	75
H-3968	300	20	$\frac{1}{15}$	500	60
g-4227	1000	8	$\frac{1}{125}$	100	8
Magnesium					
2852	500	8	$\frac{1}{60}$	100	—
4481 (+Mg)	0	20	—	50	1

¹⁴Laski, *Phys. Zeits.* xx. p. 269 (1919).

¹⁵Pringsheim, *Physik der Sonne*, p. 123.

¹⁶Evershed, *Astrophysical Journal*, vol xxv. (1909); Hale, loc. cit. vol. xxviii (1910).

Thus the tables show that in the vacuum arc the ratio Ca^+/Ca is 6-8 times its value in the ordinary arc. Unfortunately the pressure, which is a vital point, is not stated. In the case of Mg, the stimulus at the open arc is not even sufficient to excite the ionized line 4481. But a diminution in concentration brings about ionization. This case is rather remarkable because it affords an experimental basis for the view that temperature remaining the same, a diminished concentration can bring about a higher stimulus.

Conclusion

The foregoing work will probably make it clear that the theory of temperature ionization developed by the author in paper A, and more fully applied in the present paper, is capable of throwing much light on many obscure and puzzling questions of solar physics. We are precluded from making further applications owing to lack of necessary data, viz., the value of the ionization potential of elements or the value of the term or terms ($1, s$). If this and the spectral properties of all elements were known with as much certainty and exactness as in the case of alkaline earths, details of the Fraunhofer spectrum could be very satisfactorily explained.

We can, however, make the following suggestions with regard to future work on the subject:—Elements like Fe, Ti, V, Ni have probably ionization potentials varying from 6 to 9 volts, so that their behaviour is almost parallel to that of calcium and magnesium. Elements which are missing from the sun can be broadly subdivided into two groups: 1st, those which are completely ionized, e.g. Rb, Cs, and probably thallium; 2nd, elements of which the ionization and radiation potentials are so high that they are not in a state capable of absorbing those of their characteristic lines which occur in the continuous photospheric spectrum (vide paper C). Helium and most of the inert gases fall within this group. The case of helium has already been considered.

Neon, Argon¹⁷, and other inert gases have very high ionization potentials, the value being 16 volts for argon. Their principal emission lines ($1, s$)—($2, p$) lie in the ultra-violet, and identification is to be carried on by lines ($2, s$)—(m, p) or ($2, p$)—(m, d) or ($2, p$)—(m, s). As the intensity of the photospheric radiation in the region ($1, s$)—($2, p$) is very small, the compensating value of the radiation pressure is also small, and the elements fail to reach great heights. In the lower regions, the stimulus is not sufficient enough to convert the atoms to the state ($2, s$) or ($2, p$) and hence these lines do not occur in the Fraunhofer spectrum¹⁸.

The Case of the Unidentified Fraunhofer Lines.

As has been mentioned in the introduction, about 60 per cent of the Fraunhofer lines catalogued by Rowland still remain to be identified. According to Fowler, a large proportion of these are due to molecules and molecular compounds.

The best known example is the so-called cyanogen band with its head at $\lambda = 3883$, now attributed by Grotian and Runge to molecular nitrogen. Other examples are Newall's identification of the G-group of the Fraunhofer spectra with the band-lines of hydrocarbons, and Fowler's detection of ammonia and water-vapour bands in the ultra-violet part of the solar spectrum.

These identifications raise a very important point, viz., is it possible, under the conditions prevailing in the sun, for any molecule or molecular compound to exist in the undissociated state? The problems are essentially of the same nature as those which are treated by the physical chemist in the laboratory, only repeated on a scale which is not available on the earth. But thanks to the recent developments in thermodynamics by Nernst, Planck, Sackur, and others, we can now handle these problems from the theoretical side in a very satisfactory manner, if only proper data are available. Examples have already been given; it has been shown that in the sun, hydrogen and oxygen are in wholly dissociated conditions, while some proportions of nitrogen may remain in the molecular state.

The chief data which are required are heats of dissociation, the specific heat of the components, and the value of the chemical constants of the components. Thus to take a concrete case, let us consider the chemical equilibrium of NH_3 . The reaction is of the type



and the chemical equilibrium is given by the law

$$\log \frac{P^3 x^4}{(1+3x)^3(1-x)} = -\frac{U_1}{2 \cdot 3RT} + \frac{\Sigma \nu C_p}{R} \log T + \Sigma C,$$

where x is the fraction dissociated.

$$\text{Now } \Sigma \nu C_p = (C_p)_N + 3(C_p)_H - (C_p)_{\text{NH}_3}$$

$$\text{and } \Sigma \nu C = C_N + 3C_H - C_{\text{NH}_3}.$$

All of these quantities can be calculated theoretically excepting C_{NH_3} . (The theory of the chemical constant for polyatomic gases is yet to be developed—see paper mentioned below¹⁹)

It should be remembered that U_1 is different from the energy evolved in the reaction,



$$\text{if } \text{N}_2 = \text{N} + \text{N} - U_N,$$

$$\text{and } \text{H}_2 = \text{H} + \text{H} - U_H,$$

¹⁷For the spectral grouping of the lines Ne and A, see Paschen, *Ann. d. Physik.* vol. lx.

¹⁸Probably the metalloids As, Sb, Bi, etc. fall in this category, for it is well known that they can be made to emit their line spectrum at a comparatively low temperature, vide paper C, Introduction.

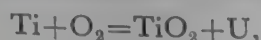
¹⁹"On the Chemical Constant of Diatomic Gases" Leon Schames, *Phys. Zeits.* vol. xxi. p. 41 (1920).

it is easy to see from the energy principle that

$$U_1 = \frac{U_N + 3U_H + U_2}{2}$$

and cannot be estimated before all these quantities are known.

For a chemical reaction of the type



the equation of chemical equilibrium is given by the formula

$$\log \frac{P^2 x^3}{(1+2x)^2(1-x)} = -\frac{U}{2 \cdot 30RT} + \frac{\sum \nu C_p}{R} \log T + \sum \nu C,$$

which reduces to

$$\log \frac{P^2 x^3}{(1+2x)^2(1-x)} = -\frac{U}{2 \cdot 30RT} + 3 \log T + C_{\text{Ti}} + 2C_{\text{O}} - C_{\text{TiO}_2},$$

if, in accordance with the kinetic theory of specific heat, we

$$\text{put } (C_p)_{\text{TiO}_2} = \frac{9R}{2}.$$

This class of chemical reaction is likely to have wide application in the treatment of the spectra of sun-spots, for a large number of spot-lines were identified by Fowler,

Hale, and Olmsted with the band-lines of MgH_2 , TiO_2 and, CaH_2 (tri-atomic compounds)²⁰.

It appears that no attention has yet been paid to the study of the spectra of the faculae, which are believed, on the basis of very sound physical arguments, to be regions of higher temperature than the photosphere. Supposing the temperature of the faculae to range between 8000°K and 9000°K, their spectra are likely to show very important differences from the spectra of the ordinary photosphere, and to be similar to the spectra of the F_0 to F_5G classes of stars, just as the spectra of sun-spots are similar to those of the Antarian stars (K-class). At any rate, the subject seems to offer a very rich field for investigation.

If the necessary data be available, these questions will be taken up in a future communication.

I have much pleasure in recording my best thanks to my students of the Post-graduate classes in physics for much useful help in preparation of this paper.

University College of Science, Calcutta.

May 22, 1920.

²⁰Pringsheim, *Physik der sonne*, pp. 211 to 217.

14. ON THE PROBLEM OF NOVA AQUILA III

(*Jour. Astr. Soc. Ind.*, **10**, 36, 1920)

The spectrum of Nova Aquila III has been studied in its various stages by many astrophysicists, all over the world, and has yielded a crop of extremely interesting results. It appears to me that in view of these results, it is now possible to seek for a plausible physical cause underlying this singular phenomenon. The results are fairly concordant and may thus be briefly summarised:

The spectrum of the Nova is a composite one and consists of four superposed spectra due to 4 distinct bodies. The first spectrum consists of bright-line emission bands of Hydrogen, Nebulium (?), Titanium, and other gases. The centres of the bands are displaced towards the red and are of enormous width. The spectrum reminds one forcibly of a pressure-shift, as mentioned by Father Cortie, (M. N. R. A. S., January 1919) and is most probably due to emission by the gases aforesaid under enormous pressure (Vide Rossi's work in Proc. Roy. Soc. Lond., Vol. 83).

Superposed upon this are three continuous spectra having

dark absorption-lines. Prof. Newall¹ finds that these spectra can be identified with that of the Star Cygni, when velocities of amounts,—1650 Km. per sec, and—2797 Km per sec are impressed upon that star. (These results are practically identical with those obtained by Evershed² and Lunt³; i.e. in other words, we are witnessing here the emission from three distinct gaseous bodies of the type of Cygni, but moving respectively with the enormous velocities of—1650 Km per sec.,—2291 Km per sec. and—2797 Km per sec. in the line of sight, but these three gaseous masses, if they really existed, had very transient existence, because none of them were recorded on Father Cortie's plate exposed on June 30th, while the emission spectrum is of much longer duration, though undergoing changes all the while.

Now I should particularly emphasise upon a point

¹ M.N.R.A.S., 1919, December.

² *Nature*, Vol 102, p 105.

³ Lunt, *The Observatory*, 1918, November.

which has been brought forward in a very lucid manner by Prof. Newall (M. N. R. A. S., December 1918). Newall compares the displacements of 50 absorption lines on a plate taken on June 13, and though they belong to elements widely differing in atomic weight, they give the same two sets of identical velocities of approach, viz., 1654 Km per sec., and—2449 Km per sec. The same may be said of the plate taken on June 15th; only here, we have evidence of three velocities of approach (—2767, —2291, —1691 Km per sec.). These observations make a very strong case for the view that we are, in this case, witnessing the emission from three distinct luminous masses of the Alpha Cygni type, which fade away to an inert non-luminous state within less than 15 days of their birth.

As stated by Dr. Lindemann (The Observatory, 1919) these huge velocities are inexplicable on any theory of explosion, while the conclusion that lines due to elements widely differing in atomic weight are displaced by amounts which can be represented by the same velocity factor is not favourable to the view of Evershed that the phenomenon has analogous features to those of eruptive solar prominences (*Nature*, Vol 102, Page 105).

It appears to me that the results obtained by Newall and supported to a large extent by Dr. Lunt in the case of Nova Germinorum (M.N.R.A.S., Feb. 1919), justify us in reviving in a modified form, the collision theory associated with the names of Huggins and Vogel. The choice of the name "Collision theory" is rather an unfortunate one. A much better appellation would be "the meteoric-flash theory". By this is meant that we are in this case witnessing a phenomenon similar to the sudden flashing up of meteorites, across our own sky—only repeated on an infinitely larger scale. It would have saved us a great deal of discussion, if we could have a consistent previous history of the star which flashed up as Nova on June 8. But this is not available. All that is known is derived from the Heidelberg and Harvard plates.

They have shown that previous to the eruption, the nova was represented by a star of 10.5 magnitude of unknown(?) parallax and spectral type, which showed rapid increment in emissive power, from June 6. No spectra seem to have been taken previous to the eruption, or shortly after the eruption was discovered (June 8. 8h. G.M.T.)

We have, accordingly, to build our hypothesis on the results of the spectra obtained during the declining stages of the Nova.

Let us suppose that the star, which represented the nova previous to the eruption, was of a compact composition (like

the red carbon stars) and enveloped in a dense atmosphere. Let us suppose that the critical velocity of escape for a particle on the surface of the star was some 2500 Km. per sec. (This is not an over-estimate, when we remember that the same quantity for our sun is some 616 Km per sec.—only it will mean a star of the same diameter but 4 times as dense). Now let a planetoid suddenly plunge into its atmosphere with a velocity equalling or exceeding the critical velocity. What would happen? A meteor, when it plunges into our own atmosphere, moves with a radial velocity of 20 to 42 Km per sec, and is heated by friction with our atmosphere through a range of more than 3000°C (from absolute zero to the temperature of the arc). Now, in the case before us, the range of temperature will be much larger. Considering the magnitude of the quantities involved, it may not be an overestimate that the outlying crusts of the planet would be heated to an incandescent gaseous mass of the Cygni type, at the same time, the planet may be torn to fragments travelling in different directions with different velocities (a sort of Roche's effect). But these luminous fragments would have a very transient existence. It appears that in the case of the Nova Aquila, the meteoric flash lasted for not less than 10 or 12 days, but it is difficult to say whether the luminous matter was left behind or whether it was carried along with any solid planetary kernel which might have survived the catastrophe. If left behind, it would diffuse through the stellar atmosphere in a short time; while if carried along with the kernel, it would be quickly reduced to the inert stage, owing to the smallness of the mass involved. At any rate, its career as a luminous body of the Alpha Cygni type could not last long. What would happen to the Star? As the planet approached it, huge tidal forces would be set up in it, causing the liberation of large amounts of gas, and as the planet flashed across, the temperature would be increased to a large extent. The star is now enveloped in a very dense atmosphere of incandescent gas, which would be responsible for the spectrum with the emission bands of enormous width.

It has been shown by Adams and Pease that Nova Auriga and Nova Persei finished up as Wolf-Rayet stars after a short nebular stage. It will be interesting to see how the Nova Aquila finishes up. At present, all the theories about the spectral types of stars are in melting pot. But if the Nova Aquila finishes up as Wolf-Rayet, I do not consider that it will be difficult to adapt the aforesaid theory to the explanation of this stage. But we must wait for the further results of spectrographic examination of the Nova in its various stages.

15. ON THE PROBLEMS OF TEMPERATURE RADIATION OF GASES (PAPER C)

(*Phil. Mag., Sr. VI*, **41**, 267, 1921)

§ 1.

The object of the present paper is to discuss and examine the present-day position of the question of temperature radiation of gases. The problem before us is, whether by simply heating a quantity of gas confined within a closed vessel (say, a silica or graphite tube), it is possible to make the gas emit its characteristic line-radiation. The experimental results on this subject are somewhat conflicting, and for different elements are widely divergent. While Pringsheim and others¹ found that permanent gases like H₂, He, Ne, A, N₂, O₂, etc. remain non-luminous even at the highest temperatures which can be commanded in the laboratory, it is known that vapours of many elements easily become luminous at moderate temperatures. Such, for example, are the vapours of I, Br, As, S, Se, Sb, and other metalloids. If we take the tube-furnace spectra of King² to be cases of pure temperature-radiation, we have to admit that at temperatures varying from 2000° to 3000°K, most of the alkalis, the alkaline earths, thallium, iron, vanadium, etc. can be made to emit their line-spectra. Gibson³ obtained the green line of thallium by simply heating the element contained in a quartz tube. But the conclusion drawn by him—that the intensity of the green line is the same as that of the black body-spectrum at this particular wave-length—is entirely wrong. He placed the quartz tube within a black-body chamber heated to about 1200°C., and observed that the continuous spectrum from the black body was crossed by a black absorption line corresponding to the green emission line. But this black line faded away as soon as the thallium vapour took up the temperature of the enclosure.

From this he concluded that the emission of the green line had just become as intense as that of the black body at the same part of the spectrum. But the conclusion is erroneous, for substances in temperature equilibrium within a black body enclosure would all emit like a black body, and the experiment proves nothing but this simple property of a black-body enclosure.

According to many physicists, the flame, the arc, and the spark represent gradually increasing stages of temperature, viz. 2000°K, 4000°K and 5000°K. It is well known that the spectra produced under these conditions are widely different

in their general characteristics, but the hypothesis that these variations can mainly be attributed to the varying values of a single physical variable, viz. the temperature, is not generally accepted.

I wish to point out that the value of the ionization potential, as obtained experimentally by Franck and Hertz, McLennan, and others, or theoretically from the quantum relation $eV = h(1, s)$, has a great bearing on the problem. As a rule, *the higher the Ionization-potential of an element, the greater is the difficulty with which it can be excited to emit its line spectrum*. This will be apparent from the following table⁴:

The line or lines $\nu = (1, s) - (2, p)$ form the most important lines of an element, and experiments on the ionization potential have shown that when the vapour of an element is bombarded by electrons, this is the line which is the first to be excited, other lines appearing only when the stimulus is substantially greater. The potential $V = \frac{h}{e} [(1s) - (2p)]$

is therefore called the resonance potential, and may be taken to be a measure of the stimulus which is required so that an element may just be excited to radiation of its fundamental line. A better name would probably be "Radiation-Potential."

We may give a number of interesting examples. It is well-known that generally it is very difficult to excite helium, the smallest trace of a foreign gas tending to quench the He-lines. According to the present theory, this is due to the fact that helium has the highest ionization and radiation potential of all elements, so that when it is subjected to a stimulus, this, by preference, passes through the more easily excitable impurities, leaving the He atoms unaffected. Franck (*Zeitschrift für Physik*, 1920, vol. i) describes an interesting experiment on the excitation, by his well-known electron bombardment method, of helium-lines contained in a tube into which a trace of mercury (less than 1 in 1000 parts) was purposely introduced. Mercury has an I.P. of 10.45 volts and R.P. of 4.9 volts, while the corresponding numbers for helium are 25.6 and 20.5. "We have then" in Franck's own words, "a strong flashing out of the lines of the element with the lower I.P., at the cost of the lines with the larger I.P."

¹Pringsheim, *Verh. d. Deutsch. Phys. Gesellschaft*, 1903. Wood, *Phys. Zeits.*, viii. (1907), and other papers.

²King, *Astro. Journal*, vols. xxviii, xxxiv, xxxv, xxxvii.

³Gibson, *Phys. Zeits.*, xii. pp. 1145-1148 (1911).

⁴McLennan, *Proc. Lond. Phys. Soc.* —Guthrie Lecture, Dec. 1918; Franck and Hertz, *Verh. d. Deutsch. Ges.* vol. xx. (1919).

TABLE I

Element	Mg	Ca	Sr	Ba	Na	K	Rb	Cs
Ionization Potential	7.65	6.12	5.70	5.21	5.11	4.32	4.16	3.88
Element	Zn	Cd	Hg	H	He	Ne	A†	N‡
Ionization Potential	9.4	9	10.45	13.6-17.1	20.5-25.6	17-23†	16	17-18

This also explains quantitatively why, with the range of temperatures available in the laboratory, it is not possible by purely thermal means to excite the permanent gases. In the case of the alkalis and the alkaline earths, the value of the ionization potential is low and gradually decreases as we proceed to elements with higher atomic weight in the same group, and it is found that the difficulty with which the spectrum can be excited lessens in a parallel manner. Thus under all conditions, if we classify the alkaline earths according to the ease with which they can be excited, the order is Ba, Sr, Ca and Mg. The same can be said of the other elements.

In the present paper I have used the word "Stimulus" to denote, in a general manner, all physical agencies tending to make the atoms luminescent. We shall discuss how a high temperature alone can bring about this state. The question can best be approached from the theoretical side.

§2

Modern spectroscopic works have shown that the lines of an element may be grouped under the following headings⁵:

(1) *Lines due to the normal atom.*—In this case the lines are produced by the quantum-changes of orbit of the outermost electron, the nucleus and the remaining electrons behaving as a single charge. The characteristic Rydberg number in the series-formula is $N \left(= \frac{2\pi^2 e^4 m}{h^3} \right)$.

These lines are produced under the comparatively low stimulus.

(2) *Lines due to the atom which has lost one electron (the outermost one).*—In this case the lines are produced by the quantum changes of orbit of the now outermost electron, the nucleus and the remaining charges behaving as a net double charge. The characteristic Rydberg number is $4N = \left\{ \frac{2\pi^2 e^2 m}{h^3} (2e)^2 \right\}$. These lines are produced at a

higher stimulus, and generally, but not always⁶, lie in the ultraviolet.

(3) The atom may lose two electrons, and now a new series of vibrations may begin with the new outermost electron. The Rydberg number is $9N$.

The lines of any of these groups are as distinct from each other as if they belong to different elements altogether. According to Sommerfeld⁷, when an atom loses one electron, its spectral properties become similar to those of the element just preceding it in the Periodic Tables. Thus the system of lines of Ca^+ are constituted in the same manner as those of K; similarly, the relation between Sr and Rb, Ba and Cs.

Lines of these different groups may be simultaneously present, but generally one group gains in intensity at the expense of the other. Thus in the flame Ca lines (the H, K) are very faint, the Ca-lines (*g*-line) is very strong. Now "*g*" begins to lose relatively in intensity as the (H, K) are strengthened with rise of temperature. At the spark-conditions, the most intense lines are the H, K, while the "*g*" is almost evanescent.

Let us now examine how the transition from the neutral state to the ionized states (from Ca to Ca^+) takes place., under the influence of heat alone. In Phil. Mag. Oct. 1920 ("Ionization in the Solar Chromosphere", called henceforth paper A), it has been shown that the problem can be attacked with the aid of the "New Thermodynamics" of Planck and Nernst⁸, and the statistical equilibrium between atoms (neutral) and ionized atoms can be calculated in terms of temperature and pressure, when the energy of ionization is known. The calculations for alkaline earths will be found in paper A, and those for the alkalis are given in paper B⁹.

According to the mechanical theory, the outermost electron of the neutral atom revolves in a stable orbit when the atom is not subject to any stimulus. Ionization means the transference of this electron to infinity. But the process is not an abrupt one, for, according to the quantum theory of spectral emission, the electron may

†Rentschler, *Phys. Rev.* vol. xiv p. 503 (1919); Horton and Davies, *Proc. Roy. Soc. Lond.* vol. xcvi. p. 124.

‡Davis and Goucher, *loc cit.*, Jan 1919; also Smyth, *loc cit.*, 1919.

⁵For example, compare Fowler's work on the "Emission Spectrum of Magnetism", *Phil. Trans.* vol. 214.

⁶For example, in case of alkaline earths. All alkaline earths are distinguished by having large ($2, p$.) terms, which causes the principal lines to occur in the visible region.

⁷Sommerfeld, *Atombau und Spektralanalyse*, Chap. 4, § 6 and Appendix.

⁸Planck, *Wärmestrahlung*; Nernst, *Das Neue Wärmesetz* etc.

⁹"Elements in the sun", *Phil. Mag.* Dec. 1920.

have an infinite number of orbits distinguished by different quanta-numbers.

The theory of stable orbits has been formulated by Sommerfeld¹⁰ in the following manner. Let n_1, n_2 denote the rotational quantum numbers for an orbit, and n' the radial quantum number, i.e. r, θ, ϕ being the coordinates of the electron: then,

$$\int \left(\frac{\partial T}{\partial r} \right) dr = n'h, \quad \int \left(\frac{\partial T}{\partial \theta} \right) d\theta = n_1 h, \quad \int \left(\frac{\partial T}{\partial \phi} \right) d\phi = n_2 h,$$

the integration extending over the whole orbit. The energy of the system is now given by the expression

$$A - h \left[\frac{N}{\{n + n' + f(n_1, n_2, n')\}^2} \right], \quad n_1 + n_2 = n,$$

where $A = a$ constant, $f(n, n')$ is a function, the value of which decreases with increasing values of n and n' .

The possible orbits can now be thus classified by assigning different sets of values to n and n' .

TABLE II

Rotational quantum No.	Radial quantum No.	Energy of the system $\frac{N}{h}$	Remarks
n	n'	i.e. $\frac{N}{\{n + n' + f(n_1, n_2, n')\}^2}$	
1 1	o $m-1$	$-(1, s)$ $-(m, s)$	This is the orbit the electron possesses when it is subject to no stimulus. $m > 1$, the s -orbits.
2 2	o $m-2$	$-(2, p)$ $-(m, p)$	The p orbits $m > 2$
3 3	o $m-3$	$-(3, d)$ $-(m, d)$	The d orbits $m > 3$
4 4	o $m-4$	$-(4, f)$ $-(m, f)$	The f orbits $m > 4$
5 5	o $m-5$	$-(5, k)$ $-(m, k)$	The k orbits $m > 5$

$(1, s), (2, p), (3, d), \dots (m, s), \dots$ are the familiar expressions which in Paschen's notation, denote the terms of which a series-formula is composed. Thus, for the principal series, the series-formula is

$$\nu = (1, s) - (m, p), \quad m \geq 2.$$

When the atom is in a free gaseous condition, and is not subject to any stimulus, it has the energy $A - h(1, s)$. The higher orbits are produced only when a stimulus is applied. The lines are emitted as the electron changes its habitat from one stable orbit to another with less energy. Thus the line $(1, s) - (2, p)$ is emitted when the electron changes its habitat from the p -orbit $(2, p)$ to the s -orbit $(1, s)$, etc. The law according to which these changes take place has been thus formulated by Rubinowicz¹¹ and Bohr.

Let n_o and n denote the rotational quantum numbers of the initial and final orbits. Then

$$n - n_o = 1, 0, \text{ or } -1.$$

We can thus distinguish among the following different types of combination:

Group I... Positive combination, $n - n_o = 1$.

$$\begin{array}{l} \text{Combination.} \left\{ \begin{array}{l} (1, s) - (m, p) \\ m \leq 2 \end{array} \right\} \left\{ \begin{array}{l} (2, p) - (m, d) \\ m \leq 3 \end{array} \right\} \left\{ \begin{array}{l} (3, d) - (m, f) \\ m \leq 4 \end{array} \right\} \\ \text{Accepted Appellation} \left\{ \begin{array}{l} \text{Principal Series} \\ \text{Diffuse Series} \\ \text{Bergmann Series} \end{array} \right\} \left\{ \begin{array}{l} (2, s) - (m, p) \\ m \leq 3 \end{array} \right\} \left\{ \begin{array}{l} (3, p) - (m, d) \\ m \leq 4 \end{array} \right\}, \text{ etc.} \end{array}$$

Group II.—Negative combination, $n - n_o = -1$

$$\begin{array}{l} \text{Combination} \left\{ \begin{array}{l} (2, p) - (m, s) \\ m \leq 1 \end{array} \right\} \left\{ \begin{array}{l} (3, d) - (m, p) \\ m \leq 2 \end{array} \right\}, \text{ etc.} \\ \text{Accepted Appellation} \left\{ \begin{array}{l} \text{Sharp Series} \end{array} \right\} \end{array}$$

Group III.—Neutral combination.

Combination... $(1, p) - (m, p), (2, p) - (m, p), (3, d) - (m, d)$

Each of the terms $(m, s), (m, p), (m, d)$ may have double or multiple values owing to the different possible orientations of the vibrating electron with regard to the remaining atom¹².

Thus far we have dealt with the electrodynamics of the atomic system, i.e. the possible stable orbits of the vibrating electron calculated according to quantum-mechanics. We have now to deal with the statistics of the case, for the higher stable orbits are produced in sufficient proportion only with increasing stimulus, which we obtain only at higher temperatures. The intensity of a line will depend upon the product of the numbers which show the relative proportions of orbits in the initial and final stages at any instant, and also upon the chance of changing from one orbit to another.

Thus the intensity of $(1, s) - (2, p)$ will be proportional to $\lambda \lambda' \epsilon$, where λ is the number of orbits in state $(1, s)$, λ' is the number in state $(2, p)$ and ϵ is the chance that the orbit will change from the state $(2, p)$ to $(1, s)$.

When the stimulus is sufficiently great, some of the electrons will pass off to infinity, and we shall have partial ionization. This problem can be treated thermodynamically, for here we have to consider a sort of chemical equilibrium between three distinct phases—the neutral atom, the ionized atom, and the electron. But radiation cannot be so treated, for this is a case of internal change of orbits only, not involving any phase-changes.

The problem before us can therefore be thus stated: "How to find out the statistical distribution of atoms into different possible stable orbits when the mass of the gas is subjected to a given thermal stimulus?" According to the theory of ionization sketched in paper A, if Ca-vapour is enclosed in a vessel, such that the pressure is always

¹⁰Sommerfeld, *Verh. d. Deutsch. Phys. Ges.*, Vol. xxi (1919).

¹¹Rubinowicz, *Phys. Zeits.*, vol. xix. pp. 441-465 (1918). Sommerfeld, *Atombau und Spektralanalyse*, pp. 390-403.

¹²For a theoretical treatment of the case, see S. N. Basu, "On the Deduction of Rydberg's Law from the Quantum Theory of Spectral Emission," *Phil. Mag.* Nov. 1919.

maintained at 10^{-3} atm., we have seen that with increasing temperature the proportion ionized varies as follows:

Temperature	2000°	3000°	4000°	5000°	6000°	7000°
Percentage of ionisation	3×10^{-4}	2×10^{-1}	6	47	91	100

The non-ionized atoms cannot all be with the primitive orbit $(1, s)$, but a good proportion will be found with the other possible stable orbits, for the electron while detaching itself from the neutral atom, has a chance of taking its habitat in some of these stable orbits, and hence some must be found in these states. The phenomena of line-radiation therefore comes before the ionization becomes complete.

§3.

At the present time, the electrodynamical part,—i.e., the manner in which the lines of an element originate from the quantum-vibrations of the constituent electrons of the atomic system—has been worked up in the case of the H-atom alone. For the other atoms, it is only in the process of making¹³.

But the thermodynamical part of the problem—that is, how the proportion of different possible stable orbits varies according to temperature, and how the orbits change from one into the other giving rise to line-radiations—has not even been clearly formulated. In his interesting development of the quantum theory applied to systems with more than one degree of freedom, Planck¹⁴ has laid the foundations of a new method for dealing with the statistical aspect of the question. The second aspect—namely, radiation following as a result of mutual interchange of stable orbits—has been dealt with by Einstein¹⁵. But there are still many difficulties to overcome. When this is done, a new and fruitful chapter—that of line radiation of gases—will be added to thermodynamics.

We may provisionally proceed along the following lines: Let us suppose that the orbits having the rotational quanta $1, 2, \dots m \dots$ vary as a geometric progression

$$(1-f) [1, f, f^2, f^3, \dots],$$

where f is a fraction and a function of temperature and concentration. Similarly, let us suppose that the orbits having the radial quanta $0, 1, 2, 3$ etc., vary according to the terms of the geometric progression

$$(1-g) [1, g, g^2, g^3, \dots],$$

where g is a similar fraction.

Then at any instant the proportion of orbits with the

rotational quantum number $n+1$ and the radial quantum number n' is

$$f^n g^{n'} (1-f) (1-g),$$

since at low temperatures and high concentrations almost the whole number of atoms is in the state $(1, s)$ corresponding to $n=1, n'=0$.

We see that f and g are very small quantities under these conditions and gradually increase as the temperature is raised or the concentration is lowered. As an example, we may take that the distribution of the Ca atoms in the orbits at 2000°K follow according to the scheme (we are considering only f here)

$$\left(1 - \frac{1}{10}\right) [1, 10^{-1}, 10^{-2}, 10^{-3} \dots],$$

while at 4000°K, the distribution is

$$(1-\frac{1}{2}) [1, \frac{1}{2}, (\frac{1}{2})^2, (\frac{1}{2})^3, \dots],$$

so that the relative intensity of the lines

$$(1, s) - (2, p), (2, p) - (3, d), (3, d) - (4, b)$$

will be $1 : 10^{-1} : 10^{-2}$, etc.;

but fully 80 percent. of the atoms will remain inactive, while at 4000°K, the ratio will be

$$1 : \frac{1}{2} : (\frac{1}{2})^2,$$

but now only 25 percent. of the non-ionized atoms remain inactive.

The above considerations are not based upon any theoretical argument, but are given here as a sort of *construierbar vorstellung* of the statistics of line-radiation of gases. We can say that, under all physical conditions, a very small concentration of radiant atoms suffices for the production of the series $\nu = (1, s) - (m, p)$, especially the fundamental line $\nu = (1, s) - (2, p)$. The $(2, p) - (m, d_i)$, $(2, s) - (m, p)$, $(3, d) - (m, f)$ lines require gradually increasing concentrations of radiant matter in addition to the condition that the stimulus should be sufficiently great. For example, if we take sodium gas at a temperature of 1500°K (an ordinary Bunsen flame tinged with sodium vapour), and gradually decrease the amount of vapour in the flame, the order in which the lines disappear are $(3, d) - (m, b)$, $(2, s) - (m, p)$, $(2, p) - (m, d)$; the $(1, s) - (m, p)$ lines, of which the leading members are the D_1 and D_2 , are the last to disappear, a fact which was recognised by Du Gramont, when he conferred the appellation "*raies ultimes*" upon this class of lines¹⁶. This state of affairs persists when the temperature is raised and gradually increasing percentages of atoms are ionized.

If a line is represented by the series formula $\nu = (n, f) - (n', f')$, the difficulty of detection of the line will be greater the larger are the values of n and n' .

In the following table we give the temperature of

¹³Sommerfeld, *Atombau und Spektralanalyse*.

¹⁴Planck, *Verh. d. D. Phys. Ges.* vol. xxii. p. 407 (1915); *Ann. d. phys.* Vol. 50. p. 385 (1916).

¹⁵Einstein, *Verh. d. D. Phys. Ges.* vol. xviii. p. 318 (1916); *Phys. Zeit.* 1918, p. 124.

¹⁶According to Bunsen and Kirchhoff, 7×10^{-12} of sodium in the Bunsen flame is quite sufficient to show the D_1 and D_2 line (Pringsheim, *Physik der Sonne*, p. 121).

complete ionization of a few elements, with the temperatures at which luminescence just begins and attains its maximum intensity. But it will be clear from what has been said that the ordinary way of speaking "the gas is heated to incandescence or luminescence just begins"—has no meaning in itself unless we say which particular line is emitted, or which orbit is produced. The orbits which are produced are specified in column 3. Under the heading "Remarks", the manner in which these temperatures have been estimated are briefly described. In this connexion, the following section on absorption should be consulted. The pressure has been taken equal to one atmosphere unless otherwise stated.

method to the other alkali metals, i.e. Potassium, Rubidium, and Caesium, and arrived at identical results. Recently Dobbie and Fox (Proc. Roy. Soc. Vol. xcvi, p. 147) studied the absorption-spectra of H₂, Zn, and Cd vapour, and found no absorption up to $\lambda=3200$. But this is due to the fact that the $(1, s)-(m, p)$ lines of these elements lie below 3000 A.U. In fact, Wood found in 1913 (Phys. Zeit. pp. 191-195) that ordinary Hg vapour absorbs the fundamental line $\lambda=2536$ $(1, s)-(2, p_2)$.

The explanation easily follows from our theory. The condition for absorption is that in the atoms present, there should be a fairly large number with orbits corresponding to the first term of the pulse of radiation to be absorbed.

TABLE III

Element	Temperature of Ionisation	Orbit generated	Luminescence begins at	Remarks	Luminescence is maximum at	Remarks
H	24,000	$(2, p)$	5,000°K	Temp. of Ma Stars	12,000°K	Temp. of Ao Stars
He	32,000	$(2, p)$	11,000°K	Temp. of A2 class	17,000°K	Temp. of B2A class
Mg ⁺	24,000	$(3, d)$	7,500°K	Temp. of Go class	11,000°K	Temp. of A2F class
Ca } Sr } Ba }	10,000-8,000°K (Pressure 10^{-1} atm.)	$(2, p)$	1,500°K	Bunsen flame	4,000°K	The open arc.

The elements N₂, O₂, A, Ne etc., resemble H₂ and He in having large values for the ionization-potential, and therefore they fail to respond to the temperatures which can be commanded in the laboratory. The alkali metals (particularly K, Rb, Cs) are more prominent in the flame-spectra and less in the arc than the alkaline earths. Mg-lines are rather faint in the flame, but come out very prominently in the open arc. Zn, Cd, Hg, Fe, Ti lie between the alkaline earths and the permanent gases in their spectral properties. All this is in very good qualitative agreement with the hypothesis sketched in the present paper.

§4. Absorption.

In this connection, we may consider the puzzling question of reversal of lines. According to Kirchhoff's law, we expect that the emission-lines of an element should be reversed when a strong beam of white light is sent through cooler layers of the vapour. But this expectation is not always fulfilled. Wood¹⁸ has found that if a white light be sent through a column of sodium vapour, only the lines of the principal pair series $(1, s)-(m, p_1)$, $(1, s)-(m, p_2)$, can be obtained as absorption-lines. None of the lines of the diffuse or the sharp series are reversed. Bevan¹⁹ has extended the

Thus, in order that a line $(2, p)-(m, d)$ may be absorbed, we must have a sufficient number of atoms with $(2, p)$ orbits. At low temperatures only atoms with $(1, s)$ orbits are present. Hence only the lines corresponding to the combination $(1, s)-(m, p)$ are absorbed. The lines represented by the positive combinations $(2, p)-(m, d)$, $(3, d)-(m, f)$, or the negative combinations $(2, p)-(m, s)$ can only occur when atoms with $(2, p)$ or $(3, d)$ orbits are present. This can happen only at high temperature or under electrical stimulus.

The temperature required for this purpose is very high—much higher than the temperatures used by Wood and Bevan for all elements. In fact, the atoms begin to absorb the lines $(2, p)-(m, d)$ only when they are not enough to emit the leading terms of the principal series. A line of the Bergmann series will begin to be absorbed at even a higher temperature, viz., at the temperature of emission of the diffuse series $(3, d)-(4, b)$.

If the views presented here be correct, we may probably obtain the reversal of the lines of the diffuse or the Bergmann series of the alkali metals by heating the absorbing column of vapour to about 2000° to 3000°K. The most favourable element to start with is caesium, which has the lowest ionization-potential of all elements.

In many cases confusion may arise about the proper identification of the $(1, s)-(m, p)$ terms. Thus, what are

¹⁸Wood, The Astrophys. Journal, vol. xxix. pp. 97-100.

¹⁹Bevan, Proc. Roy. Soc. vol. lxxxiii. pp. 423-428; vol. lxxxv. pp. 58-76.

usually called the Principal series of helium and parhelium (viz., the series beginning with the line 20,587 for parhelium and 10,834 for helium) do not really correspond to the combination $(1, s) - (m, p)$ but to the combination $(2, s) - (m, p)$. The $(1, s)$ term for helium is still unknown, and the series $(1, s) - (m, p)$ lie far down in the ultraviolet.²⁰ Hence, according to our theory, none of the lines belonging to the combinations $(2, s) - (m, p)$, $(2, p) - (m, d)$ can be absorbed by a layer of helium gas.

But if by heating or some other means we can convert a good proportion to the states $(2, s)$ or $(2, p)$, then and then only can these lines appear as absorption-lines. But at a pressure of 10^{-1} atm. helium becomes incandescent, i.e., emits the lines $(1, s) - (m, p)$, and absorbs the lines $(2, p) - (m, d)$ at probably not less than $10,000^\circ$ or $12,000^\circ\text{K}$, i.e. only in stars of the B-Class.

But instead of a high temperature we may think of other

²⁰It is quite possible that some of the $(1, s) - (m, p)$ lines for helium and parhelium may be identical with the lines discovered by Lyman in the ultra-violet, and some with the lines discovered by Richardson and Bazzoni in the region of 300 to 400 Å.U. by the photo-electric method (vide Richardson and Bazzoni, *Phil. Mag.*, 1918).

means. The spark produces mechanically the very same conditions which can be realized at very high temperatures. This is exactly what Paschen²¹ has done. He found that the lines of the combination $(2, s) - (m, p)$ for helium and parhelium cannot be absorbed by an ordinary layer of the helium gas. But when a spark is sent through the absorbing layer the lines are strongly absorbed, the absorbed energy being again re-emitted in all directions.

The paper thus suggests more problems than it attempts to solve. A critical examination and further development of the hypothesis advanced here requires an overhauling of the whole data on the line-radiation of gases—such as are contained in Kayser's *Handbuch der Spektroskopie* and further works. But this programme requires much more time and more extensive study, both practical and theoretical.

University College of Science, Calcutta.
May 25, 1920.

²¹Paschen, *Ann. d. Physik*, Vol. xlv. p. 625 (1914).

16. THE ATOMIC RADIUS AND THE IONISATION POTENTIAL

(*Nature*, **107**, 682, 1921)

Prof. Eve's interesting contribution to *Nature* of June 30, p. 552, on the relation between the ionisation potential and the atomic radius induces me to publish certain similar ideas of mine on the same subject to which I referred some time ago before the Royal Society in some remarks on Prof. Rankine's paper "On the Proximity of Atoms in Gaseous Molecules" (Proc. Roy. Soc., February, 1921). I did not publish the results, because I desired to wait for further data. These ideas may be stated as follows:—

According to the Rutherford-Bohr model of the atom, by the radius of the atom is meant the distance from the nucleus of the outermost electron, i.e. the electron the quantum vibrations of which cause the radiation of the arc lines of the atom. Sommerfeld has shown that in the normal (unexcited) state the orbit is characterised by the azimuthal quantum-number unity and the radial quantum-number zero. This orbit is circular, but to calculate its radius we must know what is the field of force exerted by the central nucleus and the remaining $(n-1)$ electrons upon the

vibrating electron. This is at present an insoluble problem, but Mr. S. N. Basu (*Phil. Mag.*, November, 1920) has shown that we can at least arrive at a qualitative explanation of Rydberg's laws of spectral regularity by assuming the attracting system to be equivalent to a net central charge unity, with a doublet of strength L . On the bases of this theory, if a_n is the radius of the monoquantic orbit, it is easy to show that

$$\frac{e^2}{2a_n} = -\text{energy of the vibrating electron.}$$

$$= h(1s) \text{ where } (1s) = \text{convergence frequency of the principal series of the element in absolute measure.}$$

$$= eV_\infty, V_\infty = \text{ionisation potential in e.s. units.}$$

For the H-atom we have, according to Bohr's theory,

$$a_H = \frac{h^3}{4\pi^2 e^2 m} \quad (a_H = \text{radius of the electron in the normal state})$$

$$= 0.532 \times 10^{-8} \text{ cm,}$$

and

$\frac{e^2}{2a_H} = e(13.54 \text{ volts})$. Therefore for an element x with an ionisation potential of V_x we have

$$a_x = \frac{(0.532 \times 13.56)}{V_x} \times 10^{-8} \text{ cm.}$$

Thus the atomic radius varies inversely as the ionisation potential.

The atomic radii calculated according to this formula are, in general, smaller than the atomic radii calculated either from crystal data (Bragg) or from the kinetic theory of gases (Rankine and others). They are shown in the appended table for the sake of comparison.

The values of V_x for copper, silver, and gold have been calculated from Hick's value of the (1S) term for these elements. That for manganese has been similarly calculated from Mr. Catalan's value of (1S) for manganese (not yet published). For these data I wish here to record my indebtedness to Prof. Fowler and Mr. Catalan. The sources for the other values are quite well known.

21 Cromwell Road,
London, July 13.

Element	I.P.	Atomic Radius		Viscosity data
		From I.P. $a \times 10^8$	Crystal measures $b \times 10^8$	
H	13.54	0.530	—	—
He	25.40	0.28	—	—
Ne	22.80	0.33	0.65	1.08
(Horton, <i>Phil. Mag.</i> , May, 1921)				
Li	5.40	1.34	1.50	—
Na	5.11	1.41	1.77	—
K	4.32	1.67	2.07	—
Rb	4.16	1.73	2.25	—
Cs	3.88	1.86	2.37	—
Cu	7.63	0.94	1.37	—
Ag	7.50	0.95	1.77	—
Au	8.63	0.83	—	—
Mg	7.61	0.95	1.42	—
Ca	6.09	1.18	1.70	—
Sr	5.67	1.27	1.95	—
Ba	5.19	1.39	2.10	—
Zn	9.35	0.77	1.32	—
Cd	8.95	0.81	1.60	—
Hg	10.38	0.69	—	—
Tl	7.30	0.90	2.25	—
Mn	7.38	0.98	1.47	—

17. ON A PHYSICAL THEORY OF STELLAR SPECTRA

(*Proc. Roy. Soc. Lond.*, **A99**, 135, 1921)

(Communicated by Prof. A. Fowler, F.R.S. Received January 18, 1921).

1. Introduction.

The present paper embodies an attempt towards a physical explanation of the ordered gradation in the spectra of stars—a subject in which pioneering work was done by the late Sir Norman Lockyer, but which was worked up with systematic thoroughness at the Harvard College Observatory, under the lead of the late Prof. E. C. Pickering and Miss A. J. Cannon.¹ During this interval the spectra of more than 100,000 stars have been photographed, classified, and published with full details in the Henry Draper Memorial Catalogue. The most noteworthy facts which have been brought to light from these monumental studies have thus been summarised by H. N. Russell.²

"The spectra of the stars show remarkably few radical differences in type. More than 99 per cent. of them fall into one or the other of the six great groups which during the classic work of the Harvard College Observatory were recognised as of fundamental importance, and received as

designations, by the process of the survival of the fittest, the rather arbitrary letters B, A, F, G, K, M. That there should be so few types is noteworthy, but much more remarkable is the fact that they form a continuous series. Every degree of gradation between the typical spectra denoted by B and A may be found in different stars, and the same is true to the end of the series, a fact recognised in the familiar decimal classification, in which B5A, for example, denotes a spectrum half-way between the typical examples B and A. The series is not merely continuous, it is linear. There exists slight difference between the spectra of different stars of the same spectral class, such as A₀, but these relate to minor details. Almost all the stars of the small outstanding minority fall into three other classes (or rather four), denoted by the letters P, O, N, R. Of these, O undoubtedly precedes B at the head of the series, while R and N, which grade one into the other, come probably at its other end, though in this case the transition stages are not clearly worked out."

Russell is of opinion that the principal differences in the stellar spectra arise in the main from variations in a single

¹Harvard, 'Annals', vol. 28, Parts I and II; vols. 56, 76, and 91.

²'Nature,' vol. 93, pp. 227, 252, 281.

physical variable in the stellar atmosphere, and many converging lines of argument show that this variable is the temperature of the stellar atmosphere. Table I shows these facts diagrammatically with provisional values of the temperature.

It is necessary to dwell a little on the physical basis of stellar classification. The earliest astrophysicists classified the stars according to colour; thus Secchi's type I denoted white stars, type II stood for yellow stars, type III for yellow-reddish stars, and type IV for deep red stars. But Lockyer and Pickering found that the varying intensity of particular groups of absorption-lines in stellar spectra was a far better criterion of stellar classification. Table II, compiled from the Harvard 'Annals', illustrates the principle.

[For the methods by means of which the intensity of a particular line in different stars has been estimated, reference should be made to Harvard 'Annals', vol. 27, p. 234; vol. 56, p. 56; vol. 91 p. 5. The following is added for the sake of general explanation:—

Numbers which are underlined denote that the line is bright; otherwise the lines are dark. Lines which are barely visible have the number 1 assigned to them. Faint lines are labelled 2. $\oplus$ denotes a line of which the intensity cannot be obtained from the Harvard 'Annals.' (?) denotes that the intensity is not stated in numbers in the Harvard 'Annals', but is compiled from descriptions scattered here

and there. The symbol M^+ denotes that the line is due to the ionised atom of the element M, *i.e.*, the atom which has lost one electron. Lockyer called them "proto" elements, and the lines were known as "enhanced lines." We shall subsequently show that they are due to the atom which has lost one electron as the result of the high temperature prevailing in the stars, and acquired a net positive charge].

The Tables show that the lines of an element just appear at a certain stage, rise step by step to a maximum, and disappear at the other end. Thus the He lines just appear at the Ao class, rise to a maximum intensity at the B3 class, and go out at the Ob class. Similarly for lines of Ca, Mg, H, and groups of nitrogen and oxygen lines not treated here because their series formulae are not known.

2. Physical Processes at High Temperatures.

The explanation of these phenomena follows from the theory of "Thermal Ionisation and Thermal Radiation" of gaseous elements developed by the author in a number of papers published elsewhere. The following is a summary.³

Up to this time thermodynamics has been confined to the treatment of physical processes like liquefaction and

³M. N. Saha, "Ionisation in the Solar Chromosphere" (A), 'Phil. Mag.', October, 1920; "Elements in the Sun" (B), December, 1920; "On the Temperature-Radiation of Gases" (C), February, 1921; "On Electron-Chemistry and its Application to Problems of Radiation and Astrophysics" (D), 'Journ. Ind. Ast. Soc.', July, 1920.

TABLE I

Stellar class	Typical star	Secchi's classification	Temperature*		Remarks
			Wilsing and Scheiner	Saha	
Pb	The Great Orion Nebula	—	15,000 K†	—	Gaseous nebulae with bright lines.
Pc	I.C., 4997	—	30,000 K	—	
Oa	B.D. +35°, 4013	Type V including Wolf-Rayet stars	23,000	23,000-24,000	
Ob	B.D. +35°, 4001		—	+22,000	Henceforth all lines are dark.
Od	ζ Puppis		—	—	
Oe	29 Canis Majoris		—	—	
Oe5	τ Canis Majoris		—	—	
Bo	ϵ Orionis	Type I, Helium and hydrogen stars	20,000	18,000	The sun is a dwarf star of this class.
B5A	η Tauri		14,000	14,000	
Ao	α Canis Majoris		11,000	12,000	
A5F	β Trianguli		9,000	—	
Fo	α Carinae		—	—	
F5A	α Canis Minor	Type II, Yellow-red stars	7,500	9,000	
Go	α Aurigae		6,000	—	
G5K	α Reticuli		5,000	7,000	
Ko	α Bootis		4,500	—	
K5M	α Tauri		4,200	—	
Ma	α Orionis	Type III, Red stars	3,200	—	
Md	α Ceti		3,100	5,000	
N	—	Type IV	2,950	4,000	
R	—		2,300	—	

* (Compiled from the Harvard 'Annals', vol. 91, p. 5, and Russel's paper, *loc. cit.* Temperatures given under the heading Saha are calculated from the method given in the present paper.)

† Buisson and Fabry, 'Journal de Physique,' 1912, p. 472 (calculated according to the limit of interference method).

TABLE II
Intensity of Stellar Lines

Element Line Series description	Helium 4471 2p-4d	4713 2p-4s	Parhe 4388 2p-5d	He ⁺ 4686 3d-4f	He ⁺ 4542 4f-9k	He ⁺⁺ 4860 4f-8k	H [*] 4860 2p-4d	Ca 4227 (g) 1s-2p	Ca ⁺ 3934 (k) 1s-2p	Mg ⁺ 4481 3d-4f
Stellar class										
Pe	—	—	—	⊕	⊕					
Pf	—	—	—	⊕	⊕					
Oa	0	—	—	⊕	⊕	⊕				
Ob	0	—	—	100	12	⊕				
Oc	1	—	—	40	3	3	0			
Od	1	—	—	20	10	20*	0	—	—	faint
Oe	15	2	3	8	5	25	10*	—	2	faint
Oe5	15	4	5	5	4	25	10	—	2	1
Bo	15	5	6	2	2	25	20	—	5	1
B2	22	6	10	1	0	35	25	—	3	2
B3	22	6	10	0	0	40	35	—	4	3
B5	10	3	7	—	—	—	40	—	4	4
B8	5	1	3	—	—	—	60	—	8	7
B9	4	0	1	—	—	—	80	faint	⊕	7 (?)
Ao	0	—	0	—	—	—	90	faint	⊕	7
A2	—	—	—	—	—	—	100	2	10	10
A3	—	—	—	—	—	—	100	4	40	15
A5	—	—	—	—	—	—	90	⊕	70	⊕
Fo	—	—	—	—	—	—	70	⊕	80	⊕
F5	—	—	—	—	—	—	50	⊕	120	⊕
Go	—	—	—	—	—	—	40	15	150 (?)	faint
G5	—	—	—	—	—	—	20	20	200	faint
Ko	—	—	—	—	—	—	15	⊕	200 (?)	0
K5	—	—	—	—	—	—	10	60	150 (?)	0
Ma	—	—	—	—	—	—	5	⊕	⊕	
Mb	—	—	—	—	—	—	2	⊕	⊕	
Mc	—	—	—	—	—	—	—	100	faint	
Md	—	—	—	—	—	—	0	strong	strong	0

*The line 4860, generally known as H β , has been shown in the Table both as a hydrogen and a He⁺ line. For reasons see footnote to Table VII, and the concluding paragraphs of §6.

vaporisation, or chemical processes like decomposition or dissociation of molecules into atoms. It has thus carried us up to the stage where all substances are broken up into constituent atoms. But what takes place if a gaseous mass consisting of atoms only be continued to be heated? Hitherto, the ideas on this point have not been very clear. In his interesting theory of internal constitution of stars, Eddington⁴ indeed suggested that in the interior of stars atoms may be, for the most part, broken up into positive nuclei and free electrons—a view which was also supported by Jeans.⁵ Following a suggestion by Nernst,⁶ Eggert⁷ tried to calculate the temperature required for tearing off the outer ring of eight electrons from the Fe-atom; he was the first to apply Nernst's theorem of the reaction-isochore (which enables us to calculate the chemical equilibrium of a dissociating system from the vapour-pressure data of the products of decomposition), to the above mentioned process of the breaking up of the Fe-atom. But not only is the

supposed process a hypothetical one, but also the energy evolved in the process, which is essential for the calculation, was obtained in a rather artificial manner. Lindemann⁸ calculated the breaking up of the H-atom into the nucleus and the electron in the solar atmosphere by using a method almost identical with that of the author, and taking the ionisation-potential=13.6 volts in accordance with Bohr's theory.

The author has shown that the first effect of increasing temperature will be to tear off the outermost electron from the atomic system, as represented in the equation,

$$\text{Ca} = \text{Ca}^+ + e - U_1. \quad (1)$$

The energy of ionisation for a gm.-atom can be exactly calculated (*i.e.*, in a way free from any hypothesis about the arrangement of electrons about the nucleus), from the ionisation-potential V_i , with the aid of the formula,

$$U_1 = \frac{eV_iN}{300J} \text{ calories.} \quad (2)$$

[N =Avogadro-number, J =mechanical equivalent of heat].

⁴Eddington, 'M.N.R.A.S.', vol. 77, pp. 16 and 596; vol. 79, p. 2.

⁵Jeans, 'M.N.R.A.S.', vol. 79, p. 319.

⁶Nernst, 'Die Theoretische und Experimentellen Grundlagen des Neuen Wärmesatzes,' 1918, p. 154, Chap. 13, concluding paragraph.

⁷Eggert, 'Phys. Zeit.,' December, 1919, p. 570.

⁸Lindemann, 'Phil. Mag.,' December, 1919.

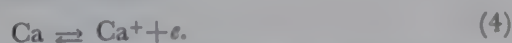
In cases where the ionisation-potential is not known from direct experimental work, it can be calculated from the convergence-frequency, $1s$, of the principal series of the element with the aid of the quantum relation⁹

$$V_i = \frac{h(1s)}{e} \cdot 300 \text{ (in volts).} \quad (3)$$

There is now very little doubt that the relation is exact. In certain cases the $1s$ -term is very large, and, as the principal series lie beyond the Schumann region, it has not been obtained at all. In such cases the $2s$ -term is often mistaken for the $1s$ -term. Helium is a well-known example. What are usually called the principal series of helium and the so-called par-helium are not $1s$ - mp series at all, but $2s$ - mp series.¹⁰ That this is so clear from the associated property that ordinary cool vapour of helium does not absorb the so-called principal series at all, but is quite transparent to them. If these were the true principal series, helium would have absorbed these lines ($\lambda=20587, 10830$, etc.), just as sodium-vapour absorbs the D_1 and D_2 lines.

Another good example is thallium, discussed by Foote and Mohler (Phil. Mag., vol. 37, p. 33.)

At a given temperature and concentration, a definite equilibrium will be established between the proportions of Ca , Ca^+ , and e , as represented by the Van't Hoff formula of reversible chemical reaction.



The equation of the reaction-isochore for calculating the equilibrium is¹¹

$$\log \frac{x^3}{1-x^2} P = -\frac{U_1}{2.3 RT} + \frac{5}{2} \log T - 6.5. \quad (5)$$

Where x =fraction ionised, P =total pressure.

Calculations for the ionisation of Ca , Sr , Ba , Mg , Na , K , Rb , Cs , H , He , will be found in the papers A and B.

The next point in question is the identification of the ionised elements in the physical systems in which they may occur. Spectroscopically¹², it is quite an easy matter, for the ionised elements show a system of lines which is quite different from the lines of the neutral atom. They are generally known as "enhanced lines." The line-system of the neutral atoms, when classified into series, have the Rydberg number $N=(2\pi^2e^4m/h^3)$, but the enhanced lines can be

grouped into series only with the Rydberg number $4N$. This fact has been very satisfactorily established for He^+ , and the alkaline earths by Fowler¹³ and Lorensen.¹⁴ It is an easy corollary from Bohr's theory of spectral emission that such lines should be due to the ionised atom.

For Zn , Cd , and Hg , Paschen and Wolff¹⁵ have discovered a number of lines in the extreme ultra-violet, which are analogous to the lines of the alkaline earths. Fues¹⁶ shows that these lines are due to the ionised atoms of the elements. For other elements, some lines are supposed to be due to the ionised atom, but these have not yet been grouped into series or critically investigated.¹⁷

At the end of §5, a Table of the chief lines of the neutral and ionised elements are given, with their series-position.

3. Physical Processes Leading to Ionisation—Radiation of the Characteristic Lines of the Neutral Atom.¹⁸

The process of ionisation cannot be an abrupt one, for the electron, in the course of passing off to infinity, can take up an infinite number of stable orbits characterised by the rotational quantum-number n , and the radial quantum number n' [$n=1, 2, 3, \dots$, $n'=0, 1, 2, \dots$], according to the Bohr-Sommerfeld¹⁹ theory of spectral emission. The various quasi-stationary orbits are represented in the following diagram, which is a slightly modified form of one given by Bohr.²⁰

In a mass of atoms, comparatively cool, and not subject to any stimulus, the atoms have their vibrating electron in the $1s$ -orbit. This orbit is circular, corresponding to $n=1$, $n'=0$, and has the energy $A-h(1s)$. This mass of gas does not emit any light, and when traversed by a continuous beam, can absorb only lines of the principal series, $v=1s$ - mp .²¹ It cannot absorb lines of the diffuse, sharp or fundamental series. But if we continue to heat up the mass, atoms will progress towards ionisation through the quasi-stationary stages represented in the following diagram, and radiation will follow as a result of the mutual interchange of orbits.²² First of all we shall have emission of

¹³Fowler, "Bakerian Lecture," 'Phil. Trans.', vol. 214.

¹⁴Lorensen, 'Inaug. Dissertation,' Tübingen, 1913.

¹⁵Paschen, 'Ann. der Physik,' vol. 35; Wolff, *loc. cit.*, vol. 42, pp. 825-839.

¹⁶Fues, 'Ann. der Physik,' vol. 63, No. 17 (1920).

¹⁷For example, the Grund-Spektren of Alkalies, discussed by Goldstein, 'Ann. der Physik,' vol. 27, p. 773; Schillinger, 'Wien. Ber.', p. 608, 1909, and Nelthorpe, 'Astrophysical Journal,' January, 1915; also the enhanced lines discussed by Lockyer and others.

¹⁸See Saha, 'Phil. Mag.,' February, 1921, "On the Temperature Radiation of Gases" (C).

¹⁹Sommerfeld, 'Atombau und Spektral-Analyse.'

²⁰Bohr, 'Zeitschrift für Physik,' vol. 2, p. 434 (1920).

²¹This fact, which comes out as a necessary corollary of the Bohr-Sommerfeld theory, has been experimentally established for Na-vapour (Wood, 'Astr. Jour.', vol. 29, p. 97; vol. 43, p. 73); for the other alkalies (Bevan, 'Roy. Soc. Proc.', A, vol. 83, pp. 821-828; vol. 84, pp. 209-225; vol. 85, pp. 54-76), and Hg (Wood, 'Phys. Zeit.', vol. 14, pp. 191-195 (1913), for cadmium (Wood, 'Astr. Jour.', vol. 29, p. 211).

²²For attempts to apply the quantum-theory to these cases, see the following papers:—Einstein, 'Phys. Zeit.', 1918, p. 124; Planck, 'Ann. der Physik,' vol. 50; 'Berliner Sitz. Ber.', 1916; 'Verh. D. Physik. G.', vol. 17 (1915).

⁹This relation, which is fundamental in the theory of the ionisation-potential, has now been definitely established for a number of elements. For a comprehensive account see McLennan, 'Proc. Phys. Soc. Lond., December, 1918; Franck and Hertz, 'Phys. Zeit.', vol. 20, p. 132 (1919).

The relation has been definitely established for:—Hg, Franck and Hertz, Davis and Goucher, 'Phys. Rev.', vol. 10, p. 101 (1917); Na, Cd, Rb, Zn, Tate and Foote, 'Phil. Mag.', vol. 36, p. 64 (1918); Mg, Tl, Foote and Mohler, 'Phil. Mag.', vol. 37, p. 33; Rb, As, Cs, Foote, Rognley, Mohler, 'Phys. Rev.', vol. 10, p. 59; Pb, Ca, Mohler, Foote, Stimson, 'Phil. Mag.', vol. 40, p. 73; Cs, Foote and Meggers, 'Phil. Mag.', vol. 40, p. 80.

¹⁰Vide Franck and Reiche, 'Ziets. f. Physik,' vol. 1, p. 154 (1920).

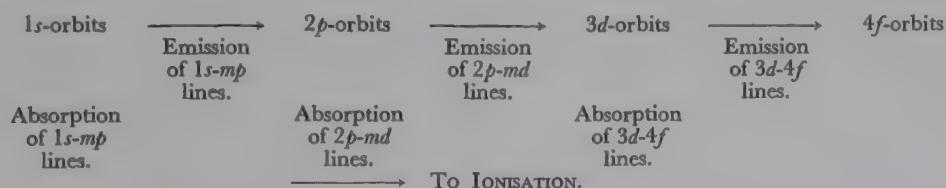
¹¹For the deduction of this formula, see Paper A, *loc. cit.*

¹²For a résumé of the early works to detect ionisation in heated gases, see McLennan, 'Roy. Soc. Proc.', A, vol. 92, p. 591. McLennan's own experiments with Hg, Zn, Cd, Tl-vapour seems to be quite inconclusive.

	Rotational quantum, n				
	1	2	3	4	n >
0	(1s)				
1	(2s)	(2p)			
3	(3s)	(3p)	(3d)		
4	(4s)	(4p)	(4d)	(4f)	
	(5s)	(5p)	(5d)	(5f)	(5k)
n'	v	v	v	v	v

To Ionisation.

1s-2p line or lines (fundamental lines), to be followed by the emission of the 1s-mp series. When the mass of gas emits the line 1s-2p rather strongly it can absorb lines of the sharp or diffuse series²³. At a further stage the 2p-md, or 2p-ms lines will begin to be emitted. The gas will now be able to absorb the fundamental series. The whole process can thus be symbolically written:—



The theory is not yet sufficiently perfect to enable us to calculate the proportion of atoms in the quasi-stationary orbits characterised by the quantum numbers n and n' ,

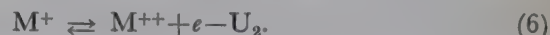
²³As a matter of fact, the 2p-ms lines, as well as the 2p-md lines, have not been reversed at all in the laboratory for any element, when the light is passed through cool vapour (J. J. Thomson, 'Phil. Mag.', April, 1919). The Balmer series of hydrogen, which may be regarded as the combined sharp and diffuse series of that element, are not reversed when continuous light is passed through ordinary H₂-vapour; but Ladenburg and Loria ('Verh. der D. Physik. G.', vol. 10. p. 858 (1908) showed that they can be obtained as reversed lines when the absorbing column of H₂ vapour is traversed by an electric current. Similarly, Paschen obtained the reversal of the so-called principal series lines of He and Parhe ($\lambda = 10830, 20587$) by passing an electric current through the absorbing column of helium-gas; ordinary helium-gas is quite transparent to these lines. This shows that the lines are not really principal lines.

but some general statements can be made.²⁴ The "radiation temperature" (*i.e.*, the temperature at which the fundamental line 1s-2p is emitted, and 2p-orbits are just commencing to form) will be higher, the higher is the ionisation-potential of the element. Other orbits will be formed at temperatures intermediate between this and the temperature at which ionisation is completed. At any stage, the proportion of atoms distinguished by the quantum numbers (n, n') will be smaller, the larger are the values of n and n' . So that we see that the 1s-2p line (and 1s-mp series) will be the first to come out, the last to go, the least amount of element will show them²⁵ and will be the most intense line all the while. The 2p-md, 2p-ms, 2s-mp lines will come out later, go out earlier, and will be increasingly fainter. The disappearance of 1s-2p line may be taken as marking the completion of ionisation.

4. Theory of Second-step Ionisation.

Let us now consider what takes place when the first-step ionisation is completed. Suppose that we have a gaseous mass consisting wholly of Ca⁺-atoms, and we continue to heat it up. It is clear that we shall have the emission of the ionised elements, *i.e.*, of the enhanced lines, followed by the commencement of a second-step ionisation, in which Ca⁺ loses another electron, and acquires a net double positive charge.

The second-step ionisation is represented by the formula



The value of U_2 is generally very large, and have not been at all experimentally investigated. But, in the case of helium and the alkaline earths, the enhanced lines have been

completely studied and grouped into series. From this we can calculate the energy of second-step ionisation by applying formula (2).

Let us suppose that the fractions x and y of the total Ca-atoms are dissociated to Ca⁺ and Ca⁺⁺-atoms

²⁴Based partly on the works of Planck and Einstein (*loc. cit.*), Planck tries to calculate the distribution of atoms in the different orbits, and Einstein considers the emission and absorption of radiant energy from the standpoint of quantum statistics. See also Epstein, "Zur Theorie des Starkeffektes," 'Ann. der Physik', vol. 50, p. 489, who considers the relative probability of passing to the quasi-stationary orbits characterised by the quantum numbers n and n' .

²⁵Cf. the experiments of Du Gramont on the "Raies Ultimes" of elements, which are either the 1s-2p line or such lines of 1s-mp series as lie in the visible region. Du Gramont, 'Bull. Soc. franc. de Phys.', 1911, No. 14.

Second-Step Ionisation.²⁶

Element	1s	Ionisation-potential	U ₂ in calories
He	4N	53.4 volts	12.3 × 10 ⁵
Mg	121,270	15.02 "	3.46 × 10 ⁵
Ca	95,740	11.86 "	2.70 × 10 ⁵
Sr	88,840	10.70 "	2.50 × 10 ⁵
Ba	80,575	9.86 "	2.30 × 10 ⁵
Zn	147,544	18.20 "	4.18 × 10 ⁵
Cd	140,226	17.30 "	3.98 × 10 ⁵
Hg	161,800 (?)	19.95 "	4.60 × 10 ⁵

respectively. Then it can be easily shown that the equation of chemical equilibrium is of the form

$$\log P \frac{x^2}{(1-x-y)(1+x+2y)} = -\frac{U_1}{2.3 RT} + \frac{5}{2} \log T - 6.5, \quad (7)$$

$$\log P \frac{y^2}{x(1+x+2y)} = -\frac{U_2}{2.3 RT} + \frac{5}{2} \log T - 6.5. \quad (8)$$

Since we are confining ourselves to the range where the proportion of neutral Ca-atoms is vanishingly small, we can put $x+y=1-\epsilon$, where ϵ is a small fraction. The equation (8) then takes the form

$$\log \frac{Py^2}{(1-y)(2+y)} = -\frac{U_2}{2.3 RT} + \frac{5}{2} \log T - 6.5. \quad (8')$$

It is no longer necessary to consider equation (7). The following Table shows the percentage of second-step ionisation of the alkaline earths at pressures of 1 and 10⁻¹ atms. Percentage of the first-step ionisation is also shown for the sake of comparison.

Table III.

Element temp.	Mg.	Mg.†	Ca.	Ca.†	Sr.	Sr.†	Ba.	Ba.†
10,000	56-90	—	85-99	8-26	90-100	14-40	94-100	23-56
11,000	75-96	—	93	18-44	95	26-64	—	40-78
12,000	86-98	—	97	31-70	98	49-89	—	59-91
13,000	93-99	10-35	99	47-86	—	61-92	—	75-96
14,000	96	21-54	—	64-93	—	76-96	—	86
15,000	98	32-72	—	81-97	—	88	—	92
16,000	99	46-85	—	87	—	92	—	96
17,000	—	61-92	—	92	—	96	—	98
18,000	—	74-96	—	95	—	98	—	—
19,000	—	83-98	—	99	—	—	—	—
20,000	—	89-99	—	99	—	—	—	—
21,000	—	93	—	—	—	—	—	—
22,000	—	96	—	—	—	—	—	—
23,000	—	98	—	—	—	—	—	—

²⁶Fowler, 'Phil., Trans.', A, vol. 214; and new calculations not yet published; Fues, 'Ann. d. Physik,' vol. 63, No. 17; Fues's figures for the 1s-terms of Zn⁺ and Cd⁺ are 159,000 and 155,000. The above figures are due to Fowler. The figure for Hg⁺ has been calculated by me by using the interesting relation that the 1s-term of the enhanced series is roughly 17/9 times the 1s-term of the neutral line system in the case of the alkaline earths, and Zn and Cd. *Vide* Fues, *loc. cit.*

In each pair of columns, the first gives the percentage of ionisation under a pressure of 1 atm., the second under a pressure of 10⁻¹ atms.

The following Table gives the ionisation of helium (both first-step and second-step) at temperatures higher than 16,000° K.

Table IV.—First-Step Ionisation of Helium.

Pressure temperature	1	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	Atm.
17,000	9	28	66	94	99	
18,000	14	41	81	97	—	
19,000	21	57	90	99		
20,000	31	71	95			
21,000	41	81	98			
22,000	53	89	99			
23,000	64	93	—			Complete.
24,000	73	96				
25,000	81	98				
26,000	87					
27,000	91					
30,000	98					

The second-step ionisation of helium is too small even in stars having the highest temperature. Consequently, He⁺ lines should be observed even when the temperature reaches 40,000°K., but actually they disappear from

Table V.—Second-Step Ionisation of Helium.

Pressure temperature	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶
24,000	—	10	24	60
25,000	—	14	39	78
26,000	—	23	57	90
27,000	10	33	72	93
28,000	17	47	86	98
29,000	26	63	95	Complete
30,000	35	77	97	"

the Pc-class of gaseous nebula, the temperature of which is not probably so high. Probably this is an effect of low pressure. According to Emden,²⁷ P=10⁻⁵ atm. in nebulae. This brings the temperature of the completion of the ionisation of He⁺ to 29,000°–30,000°K., which is not improbable.

Table VI gives the ionisation of hydrogen. It will appear from the Tables that hydrogen should definitely disappear when the temperature reaches the value 22,000°K., but this is not the case, for, according to the 'Harvard Annals,' the Balmer lines occur not only up to the Oa-class, but also in the Pa-class of nebulae, the temperature of which is probably very large.

5. Characteristic Lines of Neutral and Ionised Elements.

In § 3 we remarked that the ionised elements have a system of characteristic lines which are quite different

²⁷Emden, 'Gaskugeln,' p. 282.

Table VI.—Ionisation of Hydrogen.

Pressure temperature	1-atm.	10 ⁻¹ .	10 ⁻² .	10 ⁻³ .	10 ⁻⁴ .	10 ⁻⁵ .
7,000	—	—	—	1	4	1.5
7,500	—	—	1	3	8	12
8,000	—	—	2	5	18	26
9,000	—	2	6	20	55	44
10,000	2	5	18	49	86	89
11,000	4	13	39	80	97	
12,000	9	28	68	94		
13,000	16	45	84	98	Complete ionisation.	
14,000	27	65	93			
15,000	40	81	97			
16,000	55	90				
17,000	69	94				
18,000	80	97				
19,000	87					
20,000	92					
21,000	95					
22,000	97					
23,000	—					

from the line-system of the neutral element. Table VII shows the chief lines of both systems side by side for a few elements. Here *1s-mp*, *2p-md*, *2p-ms*, *3d-mf* respectively

stand for the principal, the diffuse, the sharp, and the fundamental series. The *1s* term is generally single, but the other terms are double, treble, or sometimes quadruple. In the principal series *m* begins with 2, in the diffuse with 3, in the sharp with 2, and in the fundamental with 4. Generally the headline of the series, and in some cases the next one or two, are given.

The principal series of hydrogen is given by the formula $\nu = N (1/1^2 - 1/m^2)$, the combined sharp and diffuse series by $\nu = N (1/2^2 - 1/m^2)$, and the fundamental series by $\nu = N (1/3^2 - 1/m^2)$. They are usually named after Lyman, Balmer, and Paschen respectively.

The classification given for helium lines is somewhat different from that usually given. The lines 20857, 5016 . . . and 10830, 3889 . . ., which are usually regarded as the principal series of parhelium and helium, are here regarded as *2s-mp* series; for reasons see § 2. The *1s*-term is, as Franck remarks²⁸, probably single, and is calculated from the ionisation-potential 25.4 volts, as experimentally obtained. The head-lines are calculated by taking *2p* from

²⁸'Zeits. f. Physik,' vol. 1, p. 154.

TABLE VII

Element	Principal <i>1s-mp</i> .	Diffuse <i>2p-md</i> .	Sharp <i>2p-ms</i> .	Fundamental <i>3d-4f</i>	Remarks
H	1215.3 (etc.).	H α 6562.8 H β 4861.3 (etc.).	—	18,751	The sharp series coincides with the diffuse series.
He	570.480 (?)	5875 4471 6678 4922	7065 4713 7281 5047	? ? —	Helium. So-called parhelium.
He ⁺	304.278 (?)	1640 1215 1087 (etc.).	—	4686	The sharp series coincides with the diffuse series as in H.
Mg	2852.11 4571.38	3838.29 32.31 29.36	5183.62 72.70 67.38		
Mg ⁺	2795.52 2802.70	2797.99 2790.77	2936.50 2928.63	4481	The 4481 line is also double.
Ca	g4226.73 6572.78				
Ca ⁺	K3933.66 H3968.47	— —	3736.90 06.02		
Sr	4607.34				
Sr ⁺	4077.88 4215.66	— —	4305.60 4161.95		
Ba	5535.69				
Ba ⁺	4554.21 4934.24				
Zn	2139.33 3075.99				
Zn ⁺	2025.57 2061.98	— —	2558.03 2502.11		
Cd	2288.79 3261.17				
Cd ⁺	2144.45 2265.13	— —	2748.68 2573.12		
Hg	1849.0 2536.72				
Hg ⁺	? —	—	2847.85 2224.70		

the parhelium terms.²⁹ Probably 570-480 may be the lines detected photo-electrically by Richardson and Bazonni.³⁰

The figures for the principal series of He^+ are calculated from the series formula $\nu=4 N (1/1^2-1/m^2)$; the lines, of course, have not been identified. The combined sharp and diffuse series lines $\nu=4 N (1/1^2-1/m^2)$ have been obtained by Lyman. The 4686 is the head-line of the Bergmann or "fundamental" combination $\nu=4 N (1/3^2-1/m^2)$. The next series combination, $4f-mk\dots$, is represented by the formula $\nu=4 N (1/4^2-1/m^2)$ and include the Pickering lines $\nu=N [1/2^2-1/(m+\frac{1}{2})^2]$ as its odd members, while the even members reduce to the Balmer formula for hydrogen, $\nu=N (1/2^2-1/m^2)$. Their wave-lengths are, however, slightly different, owing to slightly different value of N for He^+ . The intensity of these lines is also very small.³¹ The series $\nu=4 N (1/3^2-1/m^2)$ and $4 N (1/4^2-1/m^2)$ were first obtained in the laboratory by Fowler.³²

For the neutral atom of the alkaline earth group and Zn, Cd, Hg the principal lines given are those corresponding to the series combination $1S-2P$, $1S-2p_2$.³³ These are the most important lines, for experiments on ionisation-potential show that these are the first to come out when the gas is bombarded by electrons possessing the proper quantum-voltage. The ionised atoms show a system of doublets like the alkalis.

The interest of the above Table lies in the fact that it affords a possibility of spectroscopically testing the ionisation produced by a high temperature. For example, let us take a small quantity of calcium, sealed within a quartz tube which is fitted with plane ends, and then begin to heat the tube, and allow a beam of continuous light to pass through the tube. Then as soon as calcium vapour is formed, the spectrum of the transmitted beam will, on spectroscopic examination, be found to be crossed with the dark absorption lines $\lambda=4227$, $\lambda=6573$, and other associated lines of the $1S-mP$, $1S-mp_2$ series. The H, K lines will not be reversed; but if we go on increasing the temperature, then provided that the tube does not collapse, we shall find absorption lines of the diffuse and sharp series lines. Ultimately we shall find the H, K lines as reversal lines. The appearance of these lines may be taken as an indication that a good proportion of Ca atoms has become ionised.

On account of the high value of the ionisation-potential of Ca and the elements given above, it is very doubtful, however, whether experiments described above can succeed with quartz tubes or tubes of similar refractory substances known up to the present time. Experiments with the

alkali elements Cs, Rb, K are more likely to succeed, for these have very low ionisation-potentials, but the knowledge of their enhanced lines is very meagre.

In view of the total lack of laboratory data to test our hypothesis, we have to turn to the stellar data given in §1. This is done in the next section.

6. Physical Processes taking place in Stars; Temperature of Emission of the Stellar Atmospheres.

The physical meaning of the appearance and disappearance of lines given in §1, Table II, now becomes apparent. Let us start with the calcium "g" and Ca^+-K lines.

The "g" line appears in maximum intensity from the very stage when the star begins its effective life. There is no trace of the K line at the lowest stages. This just begins to appear at the Mc-stage, showing that calcium has just begun to be ionised. As we go higher up, the ionisation increases (g is fading off, K becoming more intense). The "g" line completely disappears at the B8-stage, showing that here all calcium has been ionised to Ca^+ . The K line reaches a maximum intensity at the G-5-stage, then steadily diminishes, showing that a second step ionisation has begun. It disappears completely at the Oc-stage showing that all Ca^+ has been further ionised to Ca^{++} , from above this stage.

Now referring back to Table III, we can assign the following temperatures to the points of completion of ionisation,

B8	Ca completely ionised	13,000° (Ca 1.5 p.c.)
Oc ...	Ca^+ completely ionised to Ca^{++}	20,000° (Ca^+ 1 p.c.)

and we have also at the stages

Mc...	Ca just begins to be ionised	4,000° (Ca^+ just traces).
-------	------------------------------	--------------------------------------

Go ...	Maximum proportion of Ca-atoms	7,000°
--------	--------------------------------	--------

Both Ca and Ca^+ can be identified with the aid of their fundamental lines $1s-2p$. But such is not the case with any other element excepting Sr, Sr^+ , Ba, and Ba^+ , for which we have no satisfactory data. It is well known that owing to atmospheric absorption, observations have to be confined to the spectral region $\lambda=3600$ to about $\lambda=6000$. It seems to be generally recognised, but nowhere clearly stated, that this fact alone tends to give decided preference to certain elements to the exclusion of others.

For example, let us take hydrogen. In the stars, it can be identified by the $2p-md$ lines, the $1s-mp$ lines falling within the region of atmospheric absorption. But according to § 2, the $2p-md$ lines cannot be absorbed by the ordinary H-atoms, but by such H-atoms of which the electron is in the $2p$ orbit. We can have such orbits only at high

²⁹Franck, *loc. cit.*

³⁰Phil. Mag., vol. 34, p. 285 (1917).

³¹Evans, 'Phil. Mag.', vol. 29, p. 284 (1913).

³²Phil. Trans., vol. 214.

³³Vide Fowler, *loc. cit.*

temperatures. Hence we find the Balmer lines gradually disappearing in the lower stages. We have at the stage

Mb... $2p$ -orbits of H just appearing... $T=4500^\circ$.

On the other side of the scale we find the Balmer lines of hydrogen disappearing at the Ob stage. This is an effect of complete ionisation. We have, therefore, at the stage

Ob... Complete ionisation of H... $22,000^\circ\text{C}$. (Table VI).

But if some day we can overcome the limitations imposed by the atmospheric absorbing layer, and examine stellar spectra up to $1000 \text{ \AA.U.}$, it is very probable that we shall get the Lyman lines ($1s\text{-}mp$) even at the lowest stage at which a star begins its life,³⁴ just like Calcium "g".

The disappearance of Balmer lines from a certain class therefore does not mean that hydrogen is absent from this class, but rather that the stimulus is not sufficiently great to bring out the lines lying within the range of observation.

The position of helium is quite similar. It cannot be identified by its $1s\text{-}mp$ lines, but by the $2p\text{-}md$ lines (*vide* Table VII). This can take place only when a sufficient proportion of He-atoms have been converted to the $2p$ state. Owing to the higher value of ionisation-potential of helium, this takes place, as Table II shows, at a much higher stage than that of hydrogen, viz., at the Ao stage. We have, therefore, at the stage

Ao... $2p$ -orbits of He just appearing... $T=12,000^\circ\text{K}$.

The helium line are very persistent, as Table II shows. They occur faintly in the Ob and Oa classes, and even in the gaseous nebula³⁵ up to the Pd stage. Here the transition stages have not been satisfactorily worked out. Now a glance at Table IV shows that if we take the pressure 1 atm., helium does not become completely ionised even at a temperature of $30,000^\circ$. For a pressure of 10^{-1} atm., the temperature of complete ionisation is 25000°K .

The ionisation of helium becomes marked from the B2-stage, as is shown from the appearance of the 4686 line. According to Fowler, this is the $3d\text{-}4f$ line of He^+ , and according to our theory, this requires for its absorption, not only a rather greater stimulus than that which suffices for mere ionisation, but also a greater concentration of the He^+ -atoms. We can, therefore, assign to the stage.

B2A ... Ionisation of He considerably advanced ... $T=17,000^\circ$.

I have sought in vain for satisfactory data for Mg, which can be detected by the $2p\text{-}3d$ lines only (*vide* Table VII). Mg^+ is detected by the line 4481, which, according to Fowler, has the series, combination $3d\text{-}4f$. A glance at Table II shows that, at the Go-stage, the ionisation of Mg has been considerably advanced, reaching its

completion at the Oa-stage. We have, therefore, at the stage Oa ... Mg^+ completely ionised ... $T=23,000^\circ\text{K}$.

Unfortunately, we have no data of the exact stellar classes from which the Sodium, D_1 , and D_2 lines, the Sr line 4607, the Ba line 5543, and the Mg triplet 3838, 3832, 3829, the Sr^+ 4215, 4077, and Ba 4554, 4904, ... just disappear. If these were available, they would have served as good landmarks for determining the temperature of emission of the stellar atmospheres at their various stages of evolution. If these arguments are correct, we are not justified in speaking of a star as a Hydrogen, Helium, or Carbon star, thereby suggesting that these elements form the chief ingredients in the chemical composition of the star. The proper conclusion would be that under the stimulus prevailing in the star, the particular element or elements are excited to radiation of their characteristic lines, while other elements are either ionised, or the stimulus is too weak to excite the lines by which we can detect the elements. This strikes at the root of the prevailing conception of primordial elements..

Table VIII shows the above results at a glance.

A serious discrepancy is shown by hydrogen, which, as shown by the presence of the Balmer lines, is present even beyond the Oa-stage (*vide* Table II, He^+ , 4860; we called it an He^+ line there in anticipation of the arguments which follow). But modern spectroscopic work has shown that the lines represented by the Balmer formula $\nu=N(1/2^2-1/m^2)$ cannot only be due to hydrogen, but may be due to

Table VIII.

Phenomena.	Stellar class.	Temperature.	Remarks.
Appearance of the K line	Mc	4,000 K	Beginning of the ionisation of Ca.
Disappearance of the "g" line	B8A	13,000	Ca completely ionised.
Appearance of Mg^+ 4481	Go	7,000	Mg considerably ionised.
Disappearance of the K line	Oc	20,000	Ca^+ completely ionised.
Mg^+ 4481 disappears	Oa	23,000	Mg^+ completely ionised.
Appearance of 4686	B2A	17,000	He considerably ionised.
Disappearance of 4471	Oa	24,000	He completely ionised.
Appearance of Balmer lines	Mb	(10^{-1} atm) 4,500	Appearance of the $2p$ -orbits of H.
Appearance of He lines	Ao	12,000	Appearance of $2p$ -orbits of He.
Maximum absorption of hydrogen lines	Ao	12,000	Maximum concentration of $2p$ -orbits of H.
Maximum absorption of helium lines	B2A	17,000	Maximum concentration of $2p$ -orbits of He.
Disappearance of 4295	B8A	14,000 (10^{-1} atm)	Sr^+ completely ionised.
Disappearance of Balmer-hydrogen lines	Ob	22,000	H completely ionised.
Disappearance of 4686	Pe	25,000°– 30,000°	He^+ completely ionised.

³⁴Provided, of course, the continuous spectrum from the stellar nucleus extends up to $\lambda=1000 \text{ \AA.U.}$, and is not wholly absorbed by the stellar atmosphere itself.

³⁵Harvard, 'Annals,' vol. 91, p. 5.

He⁺ and to Li⁺⁺. If the lines be due to He⁺, they should have the same intensity as the Pickering lines $\nu = 4N[1/4^2 - 1/(2m+1^2)]$, for they form the even members of the 4f-mk series of He⁺. Now, if we look back at Table II, we find that this is actually the case from the Oa- to the Oc-class, but in Od and Oe, while the Pickering lines are fading away, the Balmer lines are gaining in intensity.

This fact, taken along with the result that at 20,000°K, 10^{-1} atm. pressure hydrogen is completely ionised, leads us to the conclusion. The Balmer lines due to hydrogen disappear from the Ob-class; those occurring in the Oa-, Ob-class, are due to He⁺. In the Oc-, Od-, and Oe-class, there are blends of H and He⁺ lines, but below B2A they are entirely due to hydrogen.

The question can be settled by accurately measuring the wave-lengths of the Balmer lines in the different spectral classes, for, owing to slightly different values of N in the case of hydrogen and helium, the wave-lengths are slightly different, as the following Table shows:—³⁶

Hydrogen Lines.	He ⁺ Lines.
$\nu = N_H [1/2^2 - 1/m^2]$,	$\nu = 4N_{He} [1/4^2 - 1/(2m)^2]$.
M=1 H α , $\lambda = 6562.8$,	M=1, $\lambda = 6560.1$.
M=2 H β , $\lambda = 4861.3$,	M=2, $\lambda = 1859.3$.
M=3 H γ , $\lambda = 4340.5$,	M=3, $\lambda = 4338.7$.
M=4 H δ , $\lambda = 4101.7$,	M=4, $\lambda = 4100.0$.

The lines $\nu = N[1/2^2 - 1/m^2]$ also occur in the highest class of gaseous nebulae, Pa, which is far higher up than the class from which He⁺ disappears. There is thus a certain anomaly attached to the Balmer lines.

7. Concluding Remarks.

The work thus corroborates Russell's view that the continuous variation of stellar spectral types is mainly due to the varying values of the temperature of the stellar atmosphere, and the classification B, A, F, G, K, M, which has been adopted by the Harvard Astrophysicists, as the result of long years of study and observation, are therefore seen to acquire a new physical significance.

Some minor differences may be noted here. It appears that the temperatures assigned by Wilsing and Scheiner to stellar classes below Go are rather too low. Wilsing and Scheiner assign a temperature of 5000°K. to stars of the Go-class, of which the sun is a typical example. But Biscoe³⁷ has shown in a comprehensive work that the black-body temperature of the sun is in the neighbourhood of 7500°K.

Wilsing and Scheiner's value is therefore too low. The temperatures assigned to the K5, Ma, Md classes (3200°, 3100°, 2950°K.) are too close to each other to explain the large difference in the spectra of these types. Moreover, if these were the true temperatures, the dwarf stars of these classes would possess liquid or solid crusts consisting of carbon, tungsten, tantalum, and probably of some compounds.³⁸

From the fact that Ca⁺ first comes out in considerable quantities in the Mc class, we are probably right in assigning to this class a temperature of 4000°K. But more work is required in the spectral classification of the red stars before we can come to any definite conclusion on this point.

Adams and Kohlschütter³⁹ have recently shown that there exists considerable difference in the spectra of the giant and the dwarf stars of the same spectral class, when the intensity of certain groups of lines are compared. It will be seen from Sections 2 and 3 that the nature of the spectra is decided not only by the temperature, but also by the concentration of atoms in the stellar atmosphere. Probably the mass of the star and the average density act differently on elements of different atomic weight, so far as the concentration in the effective layer from which the absorption lines originate is concerned. The problem, however, awaits further investigation.

In spite of the uncertainty in choosing the proper concentration for a given element, it will be admitted from what has gone before that the temperature plays the leading rôle in determining the nature of the stellar spectrum. Too much importance must not be attached to the figures given, for the theory is only a first attempt for quantitatively estimating the physical processes taking place at high temperature. We have practically no laboratory data to guide us, but the stellar spectra may be regarded as unfolding to us, in an unbroken sequence, the physical processes succeeding each other as the temperature is continually varied from 3000°K. to 40,000°K.

In conclusion, it is my great pleasure to record my best thanks to Prof. A. Fowler for the interest he has taken in the work, and the many valuable items of information, advice, and criticism with which he has helped me. I also wish to express my thanks to Mr. S. K. Ghosh, M.Sc., of the Calcutta University, for much useful help in the preparation of this paper.

³⁶The melting points of tungsten and tantalum are 3800° K and 3200° K. Carbon is a volatile substance, *i.e.*, has its boiling point lower than the melting point. But Lummer claims to have succeeded in melting carbon by running the arc in an enclosed space under its own vapour pressure. He estimates the melting point to be 4200° K. under a pressure of 1 atm. of its own vapour.

³⁹Adams, 'Communications from Mount Wilson Solar Observatory,' No. 23, 1916.

³⁶Fowler, "Bakerian Lecture," 'Phil. Trans.,' A, vol. 214; Paschen, 'Ann. d. Physik,' vol. 49.

³⁷Biscoe, 'Astrophysical Journal,' vol. 46 (1917).

18. VERSUCH EINER THEORIE DER PHYSIKALISCHEN ERSCHEINUNGEN BEI HOHEN TEMPERATUREN MIT ANWENDUNGEN AUF DIE ASTROPHYSIK

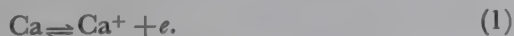
(*Zeits. f. Physik*, **6**, 40, 1921.)

Mit zwei Abbildungen. (Eingegangen am 16. Juni 1921.)

I. Einleitung.

Bis zu heutiger Zeit war die Thermodynamik in ihrer Anwendung auf physikalische Prozesse wie Schmelzen und Verdampfung, und auf chemische Prozesse, wie Zersetzung von Verbindungen, beschränkt. Was geschieht nun, wenn man eine Gasmenge, die nur aus blossen Atomen besteht, kontinuierlich erhitzt? Weder die heutige Thermodynamik sagt uns etwas über diese Frage, noch wird die Sache besser beleuchtet, wenn wir uns zur klassischen, kinetischen Gastheorie wenden, denn hier betrachten wir alle Atome als harte Kugeln, die zu weiterer Teilung unfähig sind.

Aber nach neueren wohlbekannten Untersuchungen kann man die Atome nicht immer als harte, unzerstörbare Kugeln ansehen. Es steht zweifellos fest, dass ein Atom, das im periodischen System die N -te Stelle einnimmt, aus einer Kernladung Ne , die von N Elektronen umgeben ist, besteht. Durch Beleuchtung mit ultravioletter oder Röntgenlicht oder durch Bombardieren mit schnell bewegten Elektronen kann man einige der Valenzelektronen aus dem Atomsystem entfernen (Ionisation). Nun ist leicht zu sehen, dass man denselben Prozess auch durch blosser Erhitzung erzielen kann. Bei zunehmender Temperatur stoßen die Atome öfter und mit immer grösserer Heftigkeit aneinander, bis endlich die Elektronen, eines nach dem anderen, von einem oder beiden der zusammenstossenden Atome weggeschleudert werden. So entsteht eine Anzahl freier Elektronen und positiv geladener Teilchen, die abhängig ist von der Leichtigkeit, mit welcher die Elektronen von ihren Mutteratomen getrennt werden können. Bei bestimmter Temperatur und Konzentration wird ein Gleichgewichtszustand zwischen den neutralen und den ionisierten Atomen, sowie den freien Elektronen eintreten. Wir können diesen Zustand mit der gewöhnlichen Van 't Hoff'schen Formel für das reversible chemische Gleichgewicht ausdrücken, z. B.:



Man kann das Gleichgewicht als Funktion von Temperatur und Druck berechnen, wenn man die wohlbekannte Nernst'sche Methode¹ benutzt, nach der das Gleichgewicht einer chemischen Gasreaktion von den physikalischen

Eigenschaften der beteiligten Gase abhängt. Es seien S , S' , S'' die Entropien eines Mols Ca-Dampf, Ca^+ -Dampf und Elektronendampf, ferner U die Energie der Ionisation, mit anderen Worten, die Grösse, die in der folgenden Energieformel vorkommt:

$$\text{Ca} = \text{Ca}^+ + e - U. \quad (2)$$

Wenn ein Mol Ca^+ -Gas und ein Mol Elektronengas sich bei konstanter Temperatur und konstantem Volumen zu einem Mol neutralen Ca-Gases verbinden, dann haben wir

$$S' \triangleq s - S = \frac{U}{T}. \quad (3)$$

Nach Sackur und Tetrode² ist der absolute Wert von S für ein einatomiges Gas

$$S = Nk \left[\frac{5}{2} \ln T - \ln p + \ln \frac{(2\pi m)^{3/2} k^{5/2} e^{5/2}}{h^3} \right]. \quad (4)$$

Angenommen, dass diese Formel auch für Ca^+ -Gas und für Elektronengas gilt, so kann man zeigen, dass Formel (3) sich verwandelt in

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2,3 R T} + \frac{5}{2} \log T - 6,5. \quad (5)$$

Nach (4) ist die Nernst'sche chemische Konstante

$$C = -1,602 + \frac{3}{2} \log M, \quad (6)$$

wo M =Molekulargewicht der Substanz.

Für die Elektronen ist $M = \frac{1}{1838}$; für Ca^+ -Gas hat M

denselben Wert, wie für Ca^3 .

In neuerer Zeit hat Eggerton⁴ diese Formel (6) durch Dampfdruckmessungen an Zn, Cd und Hg bestätigt. Für das Elektronengas hat M. v. Laue⁵ gezeigt, dass der Wert der chemischen Konstanten, berechnet aus Formel (6), mit den experimentellen Resultaten Langmuirs über die Emission von Elektronen aus erhitztem Wolframdraht gut übereinstimmt.

² O. Sackur, Ann. d. Phys. (4) **40**, 47, 1913; H. Tetrode, ebenda (4) **38**, 434, 1912.

³ J. Eggert, Phys. ZS. **20**, 570, 1919 [Eggert war der erste, der die chemische Konstante des Elektrons aus Formel (6) berechnet hat].

⁴ A. C. Eggerton, Phil. Mag. (6) **39**, 1, 1920; über die älteren empirischen Bestätigungen vgl. W. Nernst, Der neue Wärmesatz, S. 154.

⁵ M. v. Laue, Jahrb. d. drahtl. Telegraphie u. Telephonie **16**, 199.

¹ W. Nernst, Der neue Wärmesatz, Kapitel XI.

Wie ist nun U zu berechnen?

Man kann dieses leicht aus der von J. Franck und G. Hertz und anderen gefundenen Ionisationsspannung der Elemente berechnen mit Zuhilfenahme der Formel

$$U = \frac{e V N}{300 \bar{J}} \text{ Kalorien} \quad (7)$$

(V =Ionisationsspannung, N =die Avogadro'sche Zahl, e =die Elektronenladung, $\bar{J}$ =das mechanische Wärmeäquivalent).

Die Formel (5) gestattet uns, die Ionisation der Elemente, deren Ionisationsspannung bekannt ist, bei irgendwelchen gegebenen Werten der Temperatur und des Druckes zu berechnen. Man kann nun fragen, ob die Formel (5) als streng gültig angesehen werden kann.

Bei näherer Betrachtung zeigt sich die Formel (5) als eine erste Annäherung. Der Einfluss der zunehmenden Temperatur müsste bei dieser Betrachtung so sein, als ob der Übergang von dem neutralen zu dem ionisierten Zustand schroff vor sich geht, ohne andere dazwisch kommende physikalische Prozesse. Aber wir werden nun zeigen, dass zwischen beiden Zuständen Temperaturstrahlung stattfindet.

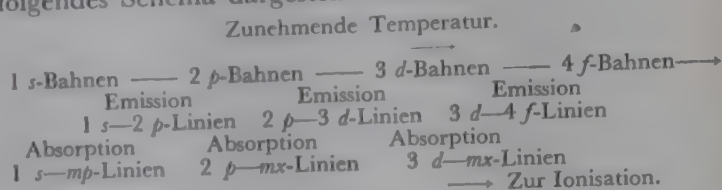
Wir wissen, dass das schwingende Elektron infolge äusserer Anregung ausser der gewöhnlichen Quantenbahn andere stabile Quantenbahnen beschreiben kann. Nach A. Sommerfeld⁶ ist die Quantenbahn des unangeregten Elektrons durch die azimuthale Quantenzahl 1 und die radiale Quantenzahl Null gekennzeichnet. Die anderen stabilen Quantenbahnen, die das Elektron im angeregten

Zustande beschreiben kann, können durch die Quantennummern n und n' gekennzeichnet werden. Daraus ist nun leicht zu ersehen, dass auf dem Wege zur Ionisation die Atome diese Quantenzustände passieren müssen. Nach N. Bohr⁷ können wir den ganzen Prozess diagrammatisch so darstellen, wie Fig. 1 zeigt.

Die Aufgabe der zukünftigen Thermodynamik wird sein, die statistische Verteilung der Atome auf diese Quantenbahnen als Funktion der Temperatur und Konzentration streng zu berechnen. Hier begnügen wir uns mit der Erörterung der Erscheinungen, die durch den oben erwähnten Prozess hervorgerufen werden.

II. Erregung und Ausstrahlung von Gasen.

Obiges führt uns zum klaren Verständnis der Erregung und Ausstrahlung von Gasen. Bei niedrigen Temperaturen befinden sich alle Elektronen der Atome in einer Gassäule nur auf der ersten Quantenbahn. Das Gas strahlt daher nicht und kann nur die Hauptlinien ($1s \rightarrow mp$) absorbieren. Bei zunehmender Temperatur geht ein Teil der Elektronen zur zweiten Quantenbahn über. Nun strahlen die Atome die Hauptlinien ($1s \rightarrow 2p$) aus und können auch die Nebelinien $2p \rightarrow mx$ absorbieren. Der ganze Prozess kann durch folgendes Schema dargestellt werden:



Daraus sehen wir, dass die Formel (3), die wir für die Berechnung der Entropie einer Gasmenge benutzt haben, nur annähernd gültig sein kann. Bei der Ableitung der Entropie einer Gasmenge aus der Quantentheorie ist stillschweigend angenommen, dass alle Atome im ersten Quantenzustand sind. Dies trifft jedoch nicht zu, und daher ist Formel (5) nur annähernd richtig. Aber solange es uns nicht gelungen ist, eine strenge Formel zu bekommen, dürfen wir nach Formel (5) verfahren.

Anwendungen. Sehen wir nun, welche Tatsachen durch die vorhergehende Theorie erklärt werden können.

(a) Temperaturstrahlung von Gasen⁸.

Die experimentellen Tatsachen über diesen Gegenstand stehen vielfach in Widerstreit und sind für verschiedene Elemente weit ausnandergehend.

F. Pringsheim⁹ und andere fanden, dass die permanenten Gase, B, H, O, N, He, A, selbst bei den höchsten Temperaturen, welche man im Laboratorium erreichen kann, nichtleuchtend bleiben. King hat viel über die sogenannten "Furnace-Spectra" gearbeitet. Ein Graphitrohr, das kleine

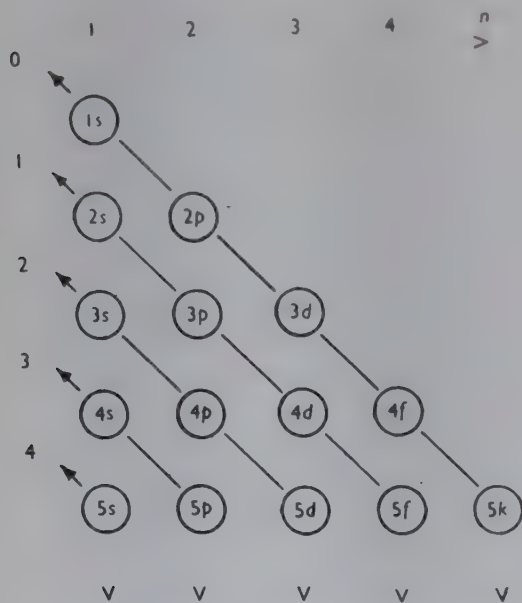


Fig. 1

⁶A. Sommerfeld, Verh. d. D. Phys. Ges. 21, 240, 1919.

⁷N. Bohr, ZS. f. Phys. 2, 423, 1920.

⁸M. N. Saha, Phil. Mag. (6) 41, 267, 1921.

⁹E. Pringsheim, Verh. d. D. Phys. Ges. 1903; R. Wood, Phys. ZS. 8, 517, 1907.

Mengen von verschiedenen Elementen, wie Ca, Sr, ... enthielt, wurde im Vakuum mit starken Wechselströmen auf Temperaturen von 2000 bis 3000° abs. gebracht und das Spektrum der dadurch verdampften Elemente beobachtet. King¹⁰ fand, dass dadurch die Alkalien, die alkalischen Erden Vanadium und Thallium, Fe usw. zur Ausstrahlung ihrer Eigenlinien gebracht werden können, und meinte, dass das Leuchten ein blosser Temperatureffekt sei. Hemsalech¹¹ stimmt darin mit ihm nicht überein und behauptet, dass dieses Leuchten durch die elektrische Anregung erfolgt.

Die gegenwärtige Theorie scheint diese vielumstrittene Frage: elektrische oder thermische Anregung, wie auch die Frage der Umkehrung von Spektrallinien aufzuklären. Nach dem Kirchhoffschen Gesetz erwartet man, dass, wenn die Dampfsäule eines Elementes mit weissem Licht durchstrahlt wird, das herauskommende Licht ein Spektrum mit allen Emissionslinien umgekehrt zeigen muss. Aber man hat gefunden, dass nur die Hauptlinien $1s \rightarrow mp$ umgekehrt sind; die Nebenlinien $2p \rightarrow md$ hat man niemals durch diese Methode umkehren können.

Nach der gegenwärtigen Theorie kann man den Misserfolg der Pringsheimschen Experimente dadurch erklären, dass er nur mit solchen Gasen gearbeitet hat, die eine sehr hohe Ionisations- und Resonanzspannung besitzen. Die Anregung, die er durch die Temperatur erzeugte, genügte nicht, um das schwingende Elektron von der ersten zur zweiten Quantenbahn zu bringen. Wie später gezeigt wird, geschieht dies beim H-Atom erst bei Sternen der M-Klasse (Temperatur etwa 4000° abs.) und beim He-Atom, wegen seiner grösseren Ionisationsspannung, erst bei Sternen der A₀-Klasse, die eine Oberflächentemperatur von etwa 10 000° abs. haben. Eng damit in Zusammenhang steht die Tatsache, dass das gewöhnliche H-Gas die Balmerlinien nicht absorbieren kann, und diese Eigenschaft erst bekommt, wenn die Gassäule von einer elektrischen Entladung erregt wird. Dieses ist eine bloss mechanische Methode, um H₂-Moleküle in Atome zu spalten und einige der Atome in die zweite Quantenbahn zu bringen. King dagegen hatte für seine Versuche nur solche Elemente gewählt, die eine niedrige Ionisationsspannung, etwa von 4 bis 9 Volt, haben; daher konnten sie bei der Temperatur, welche er benutzte, zum Leuchten gebracht werden. Der gewöhnliche Dampf von Alkalien und anderen Elementen kann die Nebenlinien nicht absorbieren, weil bei der Temperatur von 400 bis 600°C, die man benutzt hat¹², alle Atome nur im (1s)-Zustand sind. Der (2p)-Zustand, der für die Absorption der Nebenlinien nötig ist, kann nur bei höheren Temperaturen erzeugt werden.

III. Ionisation durch thermische Anregung.

Wie kann man die Ionisation erkennen?—Es gibt zwei Methoden: 1. die elektrische, 2. die spektroskopische.

1. Die elektrische Methode—elektrische Leitfähigkeit erhitzter Gase. Es ist wohlbekannt, dass eine Gassäule, die weder ultraviolettem Licht noch Röntgenstrahlen ausgesetzt ist, keine elektrische Leitfähigkeit besitzt. Viele Forscher haben Untersuchungen gemacht, um zu prüfen, ob durch Erhitzen die Gassäule leitfähig wird. Der grösste Teil dieser Untersuchungen wurde mit Quecksilberdampf gemacht und gab keine entscheidenden Resultate. Quecksilber hat eine hohe Ionisationsspannung, und daher ist nach Formel (5) die Ionisation nur 2×10^{-12} , bei einer Temperatur von 2000° und einem Drucke von 10^{-1} Atm. Die Leitfähigkeit muss daher verschwindend klein sein. Für diesen Zweck sind die Alkalien, besonders Cäsium, die geeignetsten Elemente, da sie eine geringe Ionisationsspannung besitzen. Aber es ist sehr schwer mit diesen zu arbeiten. Es gibt einen sehr alten Versuch von J. J. Thomson¹³, der die Leitfähigkeit von Na-Dampf untersuchte, aber die Temperatur war zu gering, um ein entscheidendes Resultat zu ergeben. Nach einem neueren Versuch von Hemsalech¹⁴ tritt eine merkliche Ionisation ein, wenn man die Alkalien zu folgender Temperatur erhitzt:

Li	Na	K	Rb	Cs
3000° abs.	2800° abs.	2600° abs.	2500° abs.	2200° abs.

2. Die spektroskopische Methode—Funkenspektren. Wir können die Ionisation auch spektroskopisch wahrnehmen, da die Spektren ionisierter Elemente ganz verschieden von den Spektren der neutralen Elemente sind. Die ersteren heissen „Funkenspektren“, die anderen heissen „Bogenspektren“, z. B. gehört $\lambda = 4227$, die sogenannte g-Linie, dem neutralen Ca an, die H-, K-Linien dem Ca⁺. Wenn wir in einer physikalischen Leuchtmasse—sei es eine Flamme, ein Lichtbogen oder ein Stern—die K-Linie finden, können wir sagen, dass in der Leuchtmasse Calcium ionisiert ist. Die folgende Tabelle illustriert die allmählich zunehmende Ionisation von Calcium in verschiedenen Leuchtmassen.

In ähnlicher Weise können wir auch die Ionisation anderer Elemente, von welchen die Funkenlinien bekannt sind, wahrnehmen.

Die Theorie führt uns zu einem klaren Verständnis mehrerer Tatsachen in der Astrophysik, die früher ganz unklar waren. Betrachten wir diese Tatsachen eine nach der anderen.

IV. Ionisation in der Sonnenchromosphäre¹⁵

Lockyer und Jansen war es zuerst gelungen, das chromos-

¹⁰A. S. King, *Astrophys. Journ.* **28**, **34**, **35**, **37** und andere.

¹¹G. A. Hemsalech, *Phil. Mag.* (6) **39**, 241, 1920.

¹²Zum Beispiel R. W. Wood, *The Astrophys. Journ.* **29**, 91, 1909; *Phys. ZS.* **14**, 191, 1913; P. V. Bevan, *Proc. Roy. Soc. London (A)* **86**, 320, 1912; vgl. auch J. J. Thomson, *Phil. Mag.* (6) **37**, 419, 1919.

¹³J. J. Thomson, *Phil. Mag.* (6) **9**, 584, 1905.

¹⁴S. A. Hemsalech, *C. R.* **170**, 44, 1920.

¹⁵Näheres M. N. Saha, *Phil. Mag.* (6) **40**, 472, 1920.

Tabelle 1. Ionisation des Calciums in verschiedenen Leuchtmassen.

Leuchtmasse	Temperatur	Intensität		Intensitätsverhältnis Ca/Ca ⁺
		Ca (g) $\lambda=4227$	Ca ⁺ (K) $\lambda=3934$	
Flamme	Kings	2000°	300	20
	Furnace	2500°	500	30
	Spektra	3000°	1000	60
Lichtbogen	4000°	400	500	8/10
Vakuumbogen	4000° (niederer Druck)	8	25	8/25
Photosphäre	7500°	20	1000	1/50
Chromosphäre	6000° (niederer Druck)	8	75	1/9
Sirius	10000°	Ungefähr	Hell	0
(A-Sterne)	11000°	verschunden		

phärische Spektrum allein, unter Ausschluss des Sonnenspektrums, zu photographieren und mit dem Fraunhoferschen Spektrum zu vergleichen. Nach dem Kirchhoffschen Gesetz erwartet man, dass das chromosphärische oder sogenannte „Blitzspektrum“ die Umkehrung des Fraunhoferschen Spektrums sei. Mit anderen Worten: alle Linien, die im Fraunhoferschen Spektrum dunkel erscheinen, müssen im Blitzspektrum als helle Linien auf dunklem Grunde erscheinen. Wenn man während einer totalen Sonnenfinsternis das Spektrum der Chromosphäre ohne Spalt photographiert, erhält man ein Spektrum, in welchem die hellen Linien als Bogen—das Bild der Chromosphäre—erscheinen. Aus der Länge der Bogen kann man berechnen, wie hoch ein Element—dem diese Linie angehört—sich über der Sonnenscheibe befindet. Auf diese Weise kommt man zu einer Reihe überraschender Tatsachen, die durch folgendes Diagramm (Fig. 2) dargestellt werden können.

Aus diesem Diagramm ersehen wir, dass in der Sonnenchromosphäre Ca⁺ am höchsten steht—und nicht H, das leichteste Element. Wenn man in der Chromosphäre höher steigt, verschwinden die Linien der neutralen Elemente, und nur die Linien der ionisierten Elemente, z. B. Ca⁺, Sr⁺, Ba⁺, Sc⁺, Ti⁺, ... bleiben übrig. Eine andere merkwürdige Tatsache ist, dass es in dem Fraunhoferschen Spektrum keine Spur von Heliumlinien, z. B. D₃, gibt, die Lockyer, wie wohlbekannt, zum erstenmal in der Chromosphäre fand, weshalb er sie einem auf der Erde bisher unbekannten Elemente zuschrieb und dieses nach dem griechischen Namen der Sonne Helium benannte.

Denselben Phänomenen begegnet man, wenn man die Spektren der Sterne betrachtet. In Spektren sehr heisser,

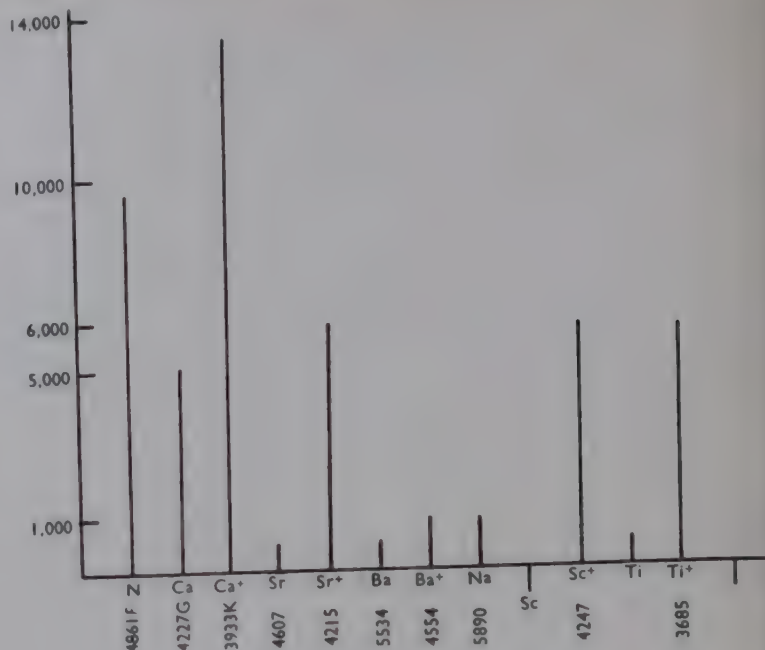


Fig. 2

z. B. der A-Sterne, werden die Bogenlinien immer schwächer, während dagegen die Funkenlinien an Helligkeit immer mehr zunehmen. Diese Tatsachen wurden zuerst von Lockyer entdeckt, aber die physikalische Ursache war ihm unbekannt. Er meinte, dass die Atome, die die Funkenlinien hervorrufen, eine frühere Form der gewöhnlichen Atome seien, und daher nur in jungen Sternen zu finden seien. Dieses führte ihn zu einer Theorie des Protoelements; z. B. ist nach Lockyer

g — 4227 die Eigenlinie des Calciums,
 K — 3934 „ „ „ Protocalciums,
 D₃ — 5876 „ „ „ Heliums,
 4686 „ „ „ Protoheliums.

Nach unserer Auffassung sind die Protoelemente nichts anderes als die ionisierten Elemente.

Wie kann man diese Tatsachen erklären? Nehmen wir zunächst die Ionisation. Da man die Funkenlinien im Laboratorium nur unter sehr starker Anregung erzielen konnte, meinte Lockyer, dass die Chromosphäre der Sitz viel stärkerer Anregung sei, als die Photosphäre. Aber wie kommt diese starke Anregung in der Chromosphäre zustande?—Lockyer meinte, dass die Chromosphäre eine höhere Temperatur als die Photosphäre hat, dass die Sonne in der Mitte kalt ist und immer heisser wird, je mehr man von innen nach aussen kommt. Diese Theorie ist durchaus unsinnig. Doch ist es bisher niemand gelungen, eine befriedigende Erklärung dieser Tatsache zu geben.

Ein Blick auf Formel (5) zeigt, dass ausser der Temperatur der Druck, die Konzentration, sehr bedeutsam für die Ionisation ist. Eine Verringerung der Konzentration wirkt in gleicher Weise, wie eine Erhöhung der

Temperatur. Dieses ist bestätigt durch die experimentellen Versuche Fowlers, dem es gelungen ist, die Mg^{+} -Linie 4481 in einem Vakuumbogen zu bekommen. In dem offenen Bogen war keine Spur dieser Linie zu finden.

Nach unserer Theorie erklärt man die zunehmende Ionisation in den höheren Lagen der Sonnenatmosphäre und das Verschwinden der neutralen Linien durch Verringerung der Konzentration, was man leicht aus der folgenden Tabelle ersehen kann.

In ähnlicher Weise kann man auch das Fehlen der Heliumlinien im Fraunhoferschen Spektrum erklären. Man kann Helium nur durch die $2p-md$ - oder $2s-mp$ -Linien wahrnehmen; dieses erfordert, dass das schwingende Elektron in die zweite Quantenbahn gebracht wird. Wegen der grossen Resonanzspannung des Heliums reicht die Anregung an der Sonnenoberfläche für diesen Zweck nicht aus, aber die Verringerung der Konzentration in der Sonnenatmosphäre ermöglicht es.

V. Vorkommen der Elemente im Sonnenspektrum¹⁶

Das Fraunhofersche Spektrum.—Es gibt noch viele Schwierigkeiten in dem Fraunhoferschen Spektrum, die man bisher nicht zu erklären vermochte. Wenn man annimmt, dass die Sonne aus denselben Elementen zusammengesetzt ist, wie die Erde, wie kommt es dann, dass im Sonnenspektrum nicht die Linien aller bekannten Elemente, sondern statt 92 nur 36 Elemente zu finden sind? Zum Beispiel findet man im Sonnenspektrum keine Linien von Rb, Cs, N, Ne, A usw. und nur sehr schwache,

TABELLE 2. Ionisation des Calciums (Prozent).

U, Energie der Ionisation = 6,12 Volt = $1,40 \times 10^5$ g-cal.
Druck in Atmosphären; Temperatur in absolutem Mass

Temperatur	Druck					
	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
3 000	—	—	—	—	$3 \cdot 10^{-1}$	1
4 000	—	—	—	3	9	26
5 000	—	2	6	20	55	90
6 000	2	8	26	64	93	99
7 000	7	23	68	91	99	—
8 000	16	46	84	97	—	—
9 000	29	70	95	99	—	—
10 000	46	85	99	—	—	—
11 000	63	93	—	Vollständige Ionisation		
12 000	76	97	—	—	—	—
13 000	84	99	—	—	—	—
14 000	90	—	—	—	—	—

etwas zweifelhafte Linien von K, Cu, O usw. Im Gegensatz dazu sind die Linien von Ca^{+} , Sr^{+} , Ba^{+} , Fe^{+} , ... ausserordentlich stark. Wie erklärt man diese Tatsachen? Man könnte sagen, dass die Sonne nur aus Ca, Na, Sr, Ba, ... besteht, und es dort kein Rb, Cs, K, Cu, ... oder nur in Spuren gibt. Aber diese Annahme ist sehr unbefriedigend und kann nur als Notbehelf betrachtet werden.

Ich bin der Meinung, dass das verschieden starke Auftreten verschiedener Elemente in dem Fraunhoferschen Spektrum hauptsächlich durch das Verhalten dieser Elemente in bezug auf die an der Sonnenoberfläche bestehende Anregung zurückzuführen ist. Die Anregung an der Sonnenoberfläche entspricht einer Temperatur von 7000 bis 7500° abs. und einem Druck von 1 bis 10^{-1} Atm. Wie verhalten sich nun die Elemente unter diesen Umständen? Betrachten wir z. B. die Alkalien, zunächst Rb und Cs. In der Sonne sind diese vollständig ionisiert. Die Linien von Rb^{+} und Cs^{+} liegen meistens im Ultraviolett, und daher entziehen sie sich unserer Beobachtung, die wegen atmosphärischer Absorption auf das Gebiet jenseits von $\lambda=3000$ beschränkt ist. Kalium ist zu 80 Proz. ionisiert und muss im Sonnenspektrum vorhanden sein, aber durch die Tatsache, dass die Hauptlinien $1s-2p$ im Ultrarot liegen, ist die Beobachtung erschwert. Das Verhandensein des Kaliums konnte durch die schwachen Linien ($1s-3p$) wahrgenommen werden, aber die Identifikation war etwas zweifelhaft. Neuerdings jedoch haben Meggers und Dutt¹⁷ durch Untersuchungen des ultraroten Teils des Sonnenspektrums diese Linien gefunden. Die Na-Linien D_1, D_2 sind in dem Fraunhoferschen Spektrum sehr stark, aber sie fehlen in den höheren Schichten der Chromosphäre, weil hier, wegen Verringerung des Drucks, Na vollständig ionisiert ist. In dem Fleckenspektrum findet man diese Linien bedeutend, etwa dreifach verstärkt, weil über den Flecken die Temperatur erniedrigt ist und der Grad der Ionisation abnimmt.

Als wichtige Folgerung aus dieser Theorie ergibt sich, dass die Sonne von einer Atmosphäre freier Elektronen umgeben ist, da in den höheren Schichten die Konzentration der positiven Teilchen gegenüber den Elektronen wegen des grösseren Gewichts des positiven Teilchens allmählich abnimmt, und die der Elektronen überwiegt wird. Wie weit sich diese Atmosphäre freier Elektronen erstreckt, und ob sie in der Lage ist, durch ihre Veränderung die terrestrischen Phänomene, wie die erdmagnetischen Schwankungen und das Nordlicht—die mit der Sonnentätigkeit eng zusammenhängen—, zu beeinflussen, muss späterer Forschung überlassen bleiben.

VI. Theorie der Spektralklassen der Sterne¹⁸

Die Theorie geht noch weiter und führt uns zum erstenmal zu einem klaren Verständnis der regelmässigen

¹⁷ W. F. Meggers, Bull. Proc. Roy. Soc. London, April 1921.

¹⁸ Näheres M. N. Saha, Proc. Roy. Soc. London (A) 99, 135, 1921.

¹⁶ Näheres M. N. Saha, Phil. Mag. (6) 41, 809, 1921.

Abstufung in den Spektren der Sterne. Frühere Astrophysiker teilten die Sterne nach ihrer Farbe in vier Klassen—weiss, gelb, rot, tiefrot—ein. Später hat man gefunden, dass die Verschiedenheiten in den Spektren der Sterne ein besseres Kriterium für die Gruppierung sind. Nach Pickering und seinen Mitarbeitern, die 35 Jahre in der Sternwarte des Harvard College sorgfältig die Spektren von ungefähr 2000 000 Sternen beobachtet haben, können die Sterne in sechs Hauptklassen gruppiert werden. Es ist sehr bemerkenswert, dass 99 Proz. der beobachteten Spektren sich in so wenige, nämlich in sechs Gruppen, einordnen lassen, aber noch bemerkenswerter ist die Tatsache, dass diese sechs Gruppen eine kontinuierliche Reihe bilden. Zwischen den typischen Spektren *A* und *B* kann man einen sehr regelmässigen Übergang feststellen, und um ein Spektrum präzise zu bezeichnen, teilt man den Zwischenraum von zwei aufeinanderfolgenden Klassen in zehn Teile ein, z. B. *B 8 A* bedeutet, dass das Spektrum acht Punkte von *B* nach *A* entfernt liegt. Die Reihe ist nicht nur kontinuierlich, sondern auch linear. Es können auch zwischen den Spektren zweier Sterne, die mit derselben Spektralunterklasse bezeichnet werden, Verschiedenheiten, aber nur in kleinen Einzelheiten bestehen. Die übrigen 1 Proz. teilt man etwas provisorisch in vier Klassen

—*O*, *P*, *N*, *R*—ein. Die Klasse *O* enthält die sogenannten Wolf-Rayetschen Sterne und muss der Klasse *B* vorgehen. *P* bedeutet Spektren von Nebeln, die nur aus hellen Linien bestehen und vielleicht der Klasse *O* vorgehen. Die Spektren der *R*- und *N*-Klasse sind sehr kompliziert und kommen vielleicht nach der *M*-Klasse.

Die Verschiedenheiten in den Spektren der Sterne, auf welche die Harvardsche Klassifikation gegründet ist, kann man leicht aus Tabelle 3 ersehen.

Aus Tabelle 3 ersieht man, dass die *g*-Linie in ihrer maximalen Intensität erscheint, wenn der Stern zuerst zu leuchten anfängt (*N*-Sterne). In diesen Klassen gibt es keine Spur der *K*-Linie (Ca^+). Diese erscheint zuerst bei den *M*-Sternen, ein Beweis, dass bei diesen Sternen Calcium ionisiert zu werden anfängt. Wenn wir höher in den Sternklassen hinaufgehen, nimmt die Ionisation zu (die *g*-Linie wird schwächer, die *K*-Linie wird stärker). Wenn wir den *B 8*-Zustand erreichen, ist die *g*-Linie ganz verschwunden. Das ist ein Beweis, dass alles Calcium vollständig ionisiert ist. Die *K*-Linie hat ihre maximale Intensität bei den *Go*-Sternen. Dann fängt Ca^+ nochmals an, ionisiert zu werden. Bei den *Oc*-Sternen verschwindet die *K*-Linie. Dies zeigt, dass alles Ca^+ zu Ca^{++} ionisiert ist.

TABELLE 3

Intensität der Sternlinien¹⁰

Element	Helium		Parhe	He ⁺	He ⁺	He ⁺	H	Ca	Ca ⁺	Mg ⁺
Linie	4471	4713	4388	4686	4542	4860	4860	4227 (<i>g</i>)	3934 (<i>k</i>)	4481
Serienbezeichnung	2 <i>p-4d</i>	2 <i>p-4s</i>	2 <i>p-5d</i>	3 <i>d-4f</i>	4 <i>f-9k</i>	4 <i>f-8k</i>	2 <i>p-4d</i>	1 <i>S-2P</i>	1 <i>s-2p</i>	3 <i>d-4f</i>
Sternklasse										
<i>Pe</i>	—	—	—	⊕	⊕	—	—	—	—	—
<i>Pf</i>	—	—	—	⊕	⊕	—	—	—	—	—
<i>Oa</i>	0	—	—	⊕	⊕	—	—	—	—	—
<i>Ob</i>	0	—	—	100	12	10	0	—	—	—
<i>Oc</i>	1	—	—	40	3	3	0	—	—	—
<i>Od</i>	1	—	—	20	10	20	10	—	2	schwach
<i>Oe</i>	15	2	3	8	5	25	10	—	2	1
<i>Oe5</i>	15	4	5	5	4	25	20	—	5	1
<i>Bo</i>	15	5	6	2	2	25	25	—	3	2
<i>B2</i>	22	6	10	1	0	35	35	—	4	3
<i>B3</i>	22	6	10	0	0	40	40	—	4	4
<i>B5</i>	10	3	7	—	—	—	60	—	8	7
<i>B8</i>	5	1	3	—	—	—	80	schwach	⊕	7 (?)
<i>B9</i>	4	0	1	—	—	—	90	schwach	⊕	7
<i>Ao</i>	0	—	0	—	—	—	100	2	10	10
<i>A2</i>	—	—	—	—	—	—	100	4	40	10
<i>A3</i>	—	—	—	—	—	—	90	⊕	70	⊕
<i>A5</i>	—	—	—	—	—	—	70	⊕	80	⊕
<i>Fo</i>	—	—	—	—	—	—	50	⊕	120	⊕
<i>F5</i>	—	—	—	—	—	—	40	15	150 (?)	schwach
<i>Go</i>	—	—	—	—	—	—	20	20	200	schwach
<i>G5</i>	—	—	—	—	—	—	15	⊕	200 (?)	0
<i>Ko</i>	—	—	—	—	—	—	10	60	150 (?)	0
<i>K5</i>	—	—	—	—	—	—	5	⊕	⊕	—
<i>Ma</i>	—	—	—	—	—	—	2	⊕	⊕	—
<i>Mb</i>	—	—	—	—	—	—	—	100	schwach	—
<i>Mc</i>	—	—	—	—	—	—	0	stark	schwach	—
<i>Md</i>	—	—	—	—	—	—	—	stark	0	—

¹⁰Das Zeichen ⊕ bedeutet, dass diese Linien beobachtet sind, aber keine Angaben über ihre Intensität vorliegen.

Nun können wir auf Grund unserer Theorie den ganzen Prozess folgendermassen beschreiben:

Bei *Mc*-Sternen .. Ca fängt an ionisiert zu werden — 4 000° abs.
 „ *G*o-Sternen .. Maximale Stärke des Ca⁺ — 7 000° „
 „ *B*8-Sternen .. Ca vollständig ionisiert .. 13 000° „
 „ *O*c-Sternen .. Ca⁺ vollständig zur Ca⁺⁺ ionisiert .. 20 000° „

Bei den anderen Elementen ist die Sachlage etwas anders. Wir können sowohl Ca als auch Ca⁺ durch ihre Resonanzlinien identifizieren, aber das ist nicht möglich für He und He⁺, H, Mg and Mg⁺. Wegen atmosphärischer Absorption sind unsere Beobachtungen auf die Grenzen zwischen $\lambda=3600$ bis $\lambda=5800$ Å.E. beschränkt. Aber Helium hat seine Resonanzlinie bei $\lambda=585$ Å.-E., Wasserstoff bei $\lambda=1216$ Å.-E., Mg bei $\lambda=2852$ Å.-E. Daher können diese Elemente nur durch die Nebenlinien—z. B. bei Helium durch die *2p—md* Linien 5878, 4471 usw., bei Wasserstoff durch die Balmerlinien (*2p—md*), bei Magnesium durch die *2p—ms*-Linien 5172, 5183 usw.—identifiziert werden. Nach unserer Theorie kann das Gasatom bei niederen Temperaturen nur die Hauptlinien *1s—mp* absorbieren. Um die Nebenlinien absorbieren zu können, muss das schwingende Elektron bei diesen Elementen in der zweiquantigen Bahn sein. Bei Wasserstoff geschieht dies zuerst bei den *Mb*-Sternen (4500°), aber bei Helium, wegen seiner grossen Ionisationsapannung, erst bei Sternen der *A*o-Klasse (12000°). Wenn wir die durch die atmosphärische Absorption verursachten Schwierigkeiten überwinden und die Sternspektren bis zum äussersten Ultraviolett verfolgen können, dann ist es sicher, dass wir auch bei kälteren Sternen (*G*, *K*, *M*) die Resonanzlinien von Helium und Wasserstoff finden können.

Die ganze Sachlage kann durch folgendes Schema dargestellt werden.

TABELLE 4.

	Stern- klasse	Temperatur	Bemerkungen
Die K-Linie erscheint	<i>Mc</i>	4 000° abs.	Ca fängt an ionisiert zu werden.
Die <i>g</i> -Linie verschwindet	<i>BSA</i>	13 000	Ca vollständig ionisiert.
Mg ⁺ 4481 verschwindet	<i>Go</i>	7 000	Mg ein wenig ionisiert.
Die K-Linie verschwindet	<i>Oc</i>	20 000	Ca ⁺ vollständig zu Ca ⁺⁺ ionisiert.
Mg ⁺ 4481 verschwindet	<i>Oa</i>	23 000	Mg ⁺ vollständig zu Mg ⁺⁺ ionisiert.
He ⁺ 4686 erscheint	<i>B2A</i>	17 000	He beträchtlich ionisiert.
He 4471 verschwindet	<i>Oa</i>	24 000 (10 ⁻¹ Atm)	He vollständig ionisiert.
Die Balmerlinien erscheinen	<i>Mb</i>	4 500	Die 2 <i>p</i> -Bahnen des Wasserstoffs erscheinen.
He 4471 erscheint	<i>B2A</i>	17 000	Die 2 <i>p</i> -Bahnen des Heliums erscheinen.
Sr ⁺ 4215 verschwindet	<i>B8A</i>	14 000 (10 ⁻¹ Atm)	Sr ⁺ vollständig zu Sr ⁺⁺ ionisiert.
Die Balmerlinien verschwinden	<i>Ob</i>	22 000	H vollständig ionisiert.
He ⁺ 4686 verschwindet	<i>Pe</i>	30 000 (10 ⁻⁸ Atm)	He ⁺ vollständig zu He ⁺⁺ ionisiert.

Tabelle 5 gibt einen einheitlichen überblick über den ganzen Entwicklungsprozess.

TABELLE 5

Sternklasse	Typischer Stern	Secchis Klassifikation	Temperatur		Bemerkungen
			Wilsing und Scheiner	Saha	
<i>Pb</i>	Gr. Orionnebel.	—	15 000 abs.	—	Gasförmiger Nebel mit hellen Linien
<i>Pc</i>	I. C., 4997	—	30 000	—	
<i>Oa</i>	B. D. +35°, 4013	Type V einschl. Wolf-Rayet- Sterne	23 000	23 000-24 000	
<i>Ob</i>	B. D. +35°, 4001		—	22 000	
<i>Od</i>	ζ Puppis		—	—	
<i>Oe</i>	29 Canis majoris	Type I Helium und Wasserstoff- Sterne	20 000	18 000	Die Sonne ist ein <i>Go</i> - Zwergstern
<i>Oe5</i>	τ Canis majoris		14 000	14 000	
<i>Bo</i>	ε Orionis		11 000	12 000	
<i>B5A</i>	γ Tauri		9 000	—	
<i>Ao</i>	α Canis majoris		7 500	9 000	
<i>A5F</i>	β Trianguli	Type II gelb-rote Sterne	6 000	7 000	
<i>Fo</i>	α Carinae		5 000	—	
<i>F5A</i>	α Canis minor		4 500	—	
<i>Go</i>	α Aurigae		4 200	—	
<i>G5K</i>	α Reticuli		3 200	—	
<i>Ko</i>	α Bootis	Type III rote Sterne	3 100	5 000	
<i>K5M</i>	α Tauri		2 950	4 000	
<i>Ma</i>	α Orionis		—	—	
<i>Md</i>	o Ceti	Type IV	—	—	
<i>N</i>	—		—	—	
<i>R</i>	—		—	—	

Schluss. Aus dem Vorhergesagten können wir schliessen, daß das Spektrum der Sterne hauptsächlich eine Funktion der Oberflächentemperatur ist, ein Schluss, der mit dem Russelschen²⁰ übereinstimmt. Ausser der Temperatur müssen wir auch die Konzentration in Betracht ziehen, und vielleicht wird es uns dadurch gelingen, die neuerdings von Adams und Kohlschütter²¹ entdeckten Verschiedenheiten in den Spektren von Riesen- und Zwergsternen derselben Klassen zu erklären.

Mangels einer strengen Theorie dürfen wir nicht den Wert, den wir für die Oberflächentemperatur der Sterne gefunden haben, für unumstösslich richtig halten, aber es möge uns gestattet sein, folgendes in allgemeiner Weise zu behaupten.

„Die typischen Sternspektren von *N* bis *O* illustrieren lückenlos die physikalischen Erscheinungen, die aufeinanderfolgen, wenn man die Temperatur allmählich von 4000° bis auf 30 000 abs. steigert.“

Wir dürfen noch einige Bemerkungen, die aus dieser Arbeit hervorgehen, hinzufügen. Sowohl in einem Stern, als auch in der Sonne ist das Spektrum eine Funktion der darin bestehenden Anregung, die überwiegend durch die Temperatur bestimmt ist. Wir haben aber gesehen, dass je nach der inneren Struktur der Atome die Temperatur die Atome in verschiedenartiger Weise anregt, z.B. bei Sternen der *Ao*. Klasse genügt die Temperatur, um Calcium fast vollständig zu ionisieren, aber sie genügt nicht, um das schwingende Elektron des Heliums von der ersten auf die zweite Quantenbahn zu bringen. Die Ionisationsspannung spielt die Hauptrolle. Wir können auch leicht sehen, dass das Fehlen der Eigenlinie eines Elements im Spektrum eines Sternes kein sicherer Beweis dafür ist, dass dieses Element in dem Sterne nicht existiert. Die Anregung mag bei Elementen, welche eine grosse Ionisationsspannung haben, zu klein sein, um sie zur Ausstrahlung ihrer Eigenlinien zu bringen (dieses ist meistens der Fall bei sogenannten permanenten Gasen, z.B. He, H, N, Ne, O usw.), oder bei Elementen, welche eine geringe Ionisationsspannung haben, mag die Anregung gross genug sein, um sie vollständig zu ionisieren (z.B. Rb und Cs auf der Sonne). Hieraus erklärt sich, dass bei sehr heissen Sternen (*O*, *B*, *A*) meistens Linien von sogenannten permanenten Gasen zu finden sind, während sie bei kälteren Sternen

schwächer werden, während die metallischen Linien allmählich heller und heller werden.

Noch eine wichtige Tatsache ist, dass wegen atmosphärischer Absorption unsere Beobachtungen bei Sternen auf die spektralen Grenzen von $\lambda=3000$ bis $\lambda=5800$ beschränkt sein müssen. Daraus folgt, dass die Elemente, deren Haupt- (oder Resonanz-) Linien in diesem Bereich liegen, eine günstige Lage für ihre Identifikation haben, da die geringste Menge des Elements genügt, um die Resonanzlinien zu zeigen, z.B. Ca und Ca^+ (Hauptlinien $g-4227$ und $K-3933$). Dagegen ist für diejenigen Elemente, die nur mit schwachen Nebenlinien $2s-mp$, $2p-md$ usw. in diesem Bereiche vertreten sind, die Lage sehr ungünstig, da man nicht nur grössere Mengen des Elements braucht, sondern auch die Atome durch Erhitzen in einen metastabilen Zustand ($2p$) gebracht werden müssen, z.B. Mg und Mg^+ (für Mg haben wir die $2p_1-3s$ -Linie 5182, für Mg^+ die Linie $3d-4f$ 481). So ist auch die Sachlage bei den sogenannten permanenten Gasen, die daher in kälteren Sternen gar nicht zu finden oder nur durch sehr schwache Linien vertreten sind.

Daraus erhellt, dass es nicht gestattet ist, aus blossen spektralen Tatsachen die Sterne als Wasserstoffsterne (*A*-Klasse) oder Heliumsterne (*B*-Klasse) oder Metallsterne (*G*-, *K*-Klasse) zu bezeichnen. Diese Art der Bezeichnung hätte den Sinu, dass die betreffenden Sterne hauptsächlich aus Wasserstoff oder Helium bestehen. Viele Astrophysiker gehen noch weiter und meinen, dass die Metalle gar nicht in der obigen Klasse von Sternen enthalten sind, die nur aus Ürelementen, wie He, H und den phantastischen Elementen Nebulium, Coronium zusammengesetzt seien, und dass die Metalle, wie Fe, Ca, Mg, sich aus diesen Ürelementen entwickelt hätten.

Auf Grund vorstehender Überlegungen ist der Gedanke, eine Theorie der Evolution der Elemente aufzustellen, ähnlich wie die Darwinsche Theorie der Evolution organischen Lebens, wohl als endgültig erledigt zu betrachten.

Zum Schluss ist es mir eine sehr angenehme Pflicht, Herrn Prof. Dr. W. Westphal, der diese Arbeit genau durchgesehen und korrigiert hat, meinen herzlichsten Dank auszudrücken. Frau M. Klutke und Herrn F. Klement spreche ich auch meinen verbindlichsten Dank aus für ihre freundliche Hilfe bei der Übersetzung ins Deutsche.

Berlin, Juni 1921.

²⁰H. N. Russell, *Nature*, **93**, 227, 252, 281, 1914.

²¹W. Adams, *Comm. Mount Wilson Solar Obs.*

19. THE STATIONARY H- AND K- LINES OF CALCIUM IN STELLAR ATMOSPHERES

(*Nature*, **107**, 498, 1921)

It has been noticed by many observers that the space surrounding early B-classes of stars (*e.g.* δ Orionis) often show absorption of H- and K-lines of calcium, which do not share in the Döpler displacements of the other absorption-lines of the stellar spectra. This suggests that these stars are enveloped in an atmosphere of calcium vapour which does not partake in the orbital motion of the stars (*NATURE*, April 21, p. 247.)

There is, of course, naturally a difficulty in realising why calcium, alone of all elements, should be found to occur in the attenuated atmospheres surrounding a stellar system. Very closely connected with this phenomenon is the observational fact that in the flash-spectrum of the sun the longest arcs are those corresponding to calcium H- and K-lines, indicating that in the sun also the outermost layers (according to Mitchell, 14,000 km. above the solar disc) are composed of calcium. Hydrogen, the lightest of elements, which we should expect to occur in the highest layers, disappears at a much lower level (8000 km., according to Mitchell).

The problem is naturally a complicated one, but I think that a way to solution is afforded by the theories of selective radiation-pressure and of the temperature-ionisation of gases advanced by me in the following papers:—"On Radiation Pressure and the Quantum Theory" (*Astrophysical Journal*, September, 1919); "On Selective Radiation Pressure, etc." (*Journ. Coll. of Science, Calcutta*, 1920); "Ionisation in the Solar Chromosphere, etc." (*Phil. Mag.*, vol. xl., 1920); and "On a Physical Theory of Stellar Spectra" (*Proc. Roy. Soc. Lond.*, May, 1921).

According to these papers, the H- and K-lines are the resonance-lines of Ca^+ , *i.e.* of a calcium-atom which has lost one electron. The resonance-line of neutral calcium is the *g*-line, $\lambda=4227$. In the Fraunhofer spectrum we get H, K, and *g*, showing that in the solar photosphere calcium is largely ionised owing to the high temperature prevailing there. At higher levels, owing to diminution in concentration, the ionisation becomes complete, so that the *g*-line disappears entirely, leaving only the H- and K-lines.

The sun is a dwarf star of the Go class, corresponding to a surface temperature of 7000-7500° K. When we consider the spectra of the still hotter stars, classes F, A, and B, we find that the *g*-line becomes fainter and fainter, until it disappears altogether from the B8A class. In the still hotter stars we have only the H- and K-lines, showing

that they do not contain neutral calcium at all, but only ionised calcium.

This explains the varying behaviour of the *g*-line and of the H- and K-lines, but we have still to determine the force which drives Ca^+ to the outermost layers. It is natural to conclude that the forces which are responsible for driving calcium absorbing H and K to the greatest height in the solar atmosphere are also responsible, in the case of stars having a larger surface temperature, for driving calcium to the surrounding parts of space. Now what can this force be, and why should this show a preference for calcium?

In the case of the sun I have attempted to show that this force is furnished by the pressure of radiant energy from the solar disc acting in a selective way upon the Ca^+ -atoms. The term "selective" is most important here and requires an explanation. Radiation-pressure is due to absorption, and therefore, in the case of a gas illuminated by white light, only those pulses which the gaseous atom is capable of *most frequently absorbing* are effective in producing pressure. A gas can usually absorb lines of the principal series alone, but the lines of the subordinate series are absorbed only in exceptional circumstances, and even then to a much smaller extent; so that the maximum lifting effect of radiation-pressure is to be expected only in the case of atoms absorbing the resonance-lines. (For more detailed arguments see the papers above-mentioned). In addition to this, the lifting force would depend on the intensity of the region corresponding to the absorbed lines in the spectrum of the continuous background of white light, and on the solid angle subtended at the atom by this background.

In the case of the sun the surface temperature is 7300-7500°K (Biscoe, *Astrophysical Journal*, vol. xlv., p 355), so that, according to Wien's law, $\lambda_m T = b$, the maximum of emission lies at $\lambda=3920$ Å.U., very close to the H- and K-lines of Ca^+ . Also these lines are the resonance-lines of Ca^+ , so that we have here the maximum effect of selective radiation-pressure. The resonance-line of hydrogen is at $\lambda=1216$ Å.U., and therefore the effect of radiation-pressure is extremely small.

It is not possible to say whether the lifting power of selective radiation-pressure alone is capable of neutralising the force due to the gravitational attraction of the sun, but it looks very much as if this were so. Without being dogmatic on this point, we can work out the consequences of this assumption. In the case of stars having a much

larger surface temperature, say 14,000°K, B8A class, the value $E\lambda$ for H- and K-light would be much larger, so that the radiation-pressure is still greater, and in some cases preponderates over the greater value of gravitational force on these stars. Thus Ca^+ -atoms would be driven very far into the surrounding space. They will be prevented from absolutely leaving the system, because with increase of distance the solid angle subtended by the disc of the star at the atom would diminish, and a condition of equilibrium would at last be reached.

The same phenomenon occurs to a smaller extent, in the case of the sun, with Sr^+ and Ba^+ , which have their resonance-lines near the spectral region of maximum intensity, but owing to their greater atomic weight the compensation is not so marked. Still Sr^+ is very prominent in the chromospheric spectrum, rising to a height of 6000 km.

The question may be asked: Why do we not obtain the same phenomenon in the case of the other light elements? These can be divided into two broad groups: (1) non-metals like H, He, N, O, Ne, and A, having a high ionisation-potential, of which the resonance-lines lie in the extreme ultra-violet—*e.g.* for H, at $\lambda=1216 \text{ \AA.U.}$, for He, at $\lambda=585 \text{ \AA.U.}$ (Lyman and Fricke, *Phil. Mag.*, May, 1920)—and can be detected only by subordinate lines—for helium, by D_3 , $2p-md$; for hydrogen, by the Balmer lines. Naturally the effect of selective radiation-pressure is small on these elements. (2) Elements like Na, K, Mg, Al, Sc, Ti, Fe, which have an ionisation-potential varying from 5 to 8 volts. Under the conditions treated here these are mostly ionised, but the resonance-lines of these ionised elements lie mostly outside the region available for observation,

e.g. the resonance-lines of Mg^+ are $\lambda=2795.5, 2802.7$. The resonance-lines of Na^+ and K^+ have not yet been discovered, and probably lie in the extreme ultra-violet. Sc^+ and Ti^+ are represented by prominent lines in the chromospheric spectrum, but it is not yet known whether these are resonance-lines of these elements.

The hypotheses thus appear to be promising, but nothing final can be said before we can calculate the absolute value of the selective radiation-pressure on an atom. According to Eddington (*Monthly Notices, R.A.S.*, 1920, vol. lxxx., p. 723), the absolute value of the radiation-pressure is too small to account for the total neutralisation of gravitational force on the sun; but in that paper the consequences are worked on the basis of the continuous theory of light. The foregoing line of investigation at least brings out the intimate connection between the stationary character of the H- and K-lines in the space round the stars and the great prominence of these lines in the chromospheric spectrum. It shows that the higher chromospheric levels, as well as the space round B- and A-stars, may probably contain, besides Ca^+ , also Na^+ , K^+ , Sc^+ , Ti^+ , and Mg^+ , but owing to the fact that our observations have to be limited between $\lambda=3000 \text{ \AA.U.}$ and $6000 \text{ \AA.U.}$, and that none but the resonance-lines of Ca^+ lie within this region, we can detect nothing but Ca^+ . But if some day we can overcome the limitation imposed by atmospheric absorption, probably we shall be able to detect Li^+ , Na^+ , Mg^+ , K^+ in the atmospheres surrounding B-stars which show stationary H- and K-lines.

Berlin, May 8.

20. ON THE IONISATION OF GASES BY HEAT

M. N. SAHA AND PAUL GUNTHER

(*Jour. Dept. Sci.*, Cal. Univ., 4, 97, 1922)

§ 1. INTRODUCTION

It is well known that a column of gas, which is subjected neither to ultraviolet light, Röntgen light, or any other familiar ionising agent, possesses no electrical conductivity. Beginning from Hittorf¹ many investigators have performed experiments to see, if by simple heating, gases can be made to conduct electricity. As the following review will show, most of these experiments were indecisive.

In the light of modern theories of atomic structure,

the problem reduces to the knocking out of the outermost electron, or electrons, from the atomic system by the mutual collisions of atoms. The problem is thus analogous to the emission of electrons from incandescent solids and liquids. In this connection, it is well worth quoting the following passage from Richardson's "The Emission of Electricity from Hot Bodies, p. 298."

"There is no satisfactory *a priori* reason for expecting emission of ions at a high temperature to be confined to the matters in solid or liquid states. It is however to be

anticipated that the thermal ionisation of gases will only be appreciable at the very highest temperatures, on account of the large value of the ionisation energy of gases. This quantity which has been measured by experiments on impact ionisation and photoelectrical action, has in all cases been found to be much greater than the energy changes governing the liberation of an ion in the phenomena which have been considered in this book. Up to the present there is no evidence that purely thermal ionisation has been observed in any of the common gases. It seems likely that the ions present in flames, are to be attributed to the chemical actions occurring rather than to the direct effect on the gases of the high temperature which prevails. In the case of gases which have been heated in the presence of metal electrodes, there is no evidence of the formation of ions except by interaction between the gases, and the electrodes or by the emission from the electrodes themselves.

A possible exception to these statement is furnished by some experiments made by J. J. Thomson² on sodium vapour. He found that when a current was made to pass between two electrodes immersed in this vapour at about 300°C, metallic sodium collected on the negative, but not on the positive electrode, indicating that the sodium atoms in the vapour has dissociated into an electron and a positive sodium ion. The phenomenon could also be accounted for if the bombardment of the positive electrode by electrons present made it hotter than the negative electrode. The optical properties of sodium vapour make it probable that it will dissociate, in the manner indicated, below 1000°C. It is necessary to add that Thomson's experiments have been repeated by Fredenhagen (Phys. Zs. Bd. XII, p. 398, 1911), without success; so that it does not seem absolutely certain that the phenomenon has yet been discovered."

Another series of experiments have been made on mercury vapour to discover this effect. We take the following history of these experiments from a paper by McLennan (Proc. Roy. Soc. Lond., Vol. 92, p. 592).

"Though numerous investigators have experimented on the electrical conductivity of salts of different metals in flames, but few appear to have made a study of the conductivity of the vapours of the simple metals themselves. Hittorf, who investigated the conductivity of the mercury vapours by heating the metal in a tube and passing the discharge from an induction coil through it came to the conclusion that it was nonconducting. Herweg however found that mercury vapour, when heated to 1000°C. did exhibit electrical conductivity.

Sir J. J. Thomson also found that mercury vapour, even at a very high temperature was a good insulator, a better one in fact than air, under the same conditions. Strutt, who investigated the electrical conductivity of mercury vapour in an evacuated quartz tube heated to redness, also found it to be an insulator."

In the paper just mentioned, McLennan and Keys

investigated the conductivity of vapours of mercury, cadmium, zinc and thallium, in a Bunsen flame, but the results were very much discordant. Mercury seemed to be ionised, but zinc and cadmium showed absolutely no trace of ionisation. The ionisation potential of these elements are respectively 9.4, 9.00 and 10.45 volts, so that if the observed conductivity of mercury vapour arose from the heat ionisation, there is no reason why zinc and cadmium vapours would not be ionised under the same conditions. McLennan himself concludes that the experimental results were quite indecisive.

§ 2

The effect may therefore be regarded as yet experimentally undiscovered.

It follows *a priori* that the chance of success depends to a large extent on the choice of the right substance for experimental work. The force with which the outermost electrons are bound to the parent atomic system is different in different elements. In the case when the elements are in the solid state of aggregation, the measure of this force is the quantity ' ϕ ' in Richardson's equation for thermoelectric emission $i = AT^{\frac{1}{2}} e^{-\frac{\phi}{kT}}$. In the case of gases the force can now be measured with great accuracy either from spectroscopic data or from the experimental works³ on ionisation-potential. It is known from these works that of all elements, Caesium is the one having the least ionisation potential, *viz.*,—3.88 volts and then follows the other alkali metals in the reverse order of their atomic weights, *e.g.*, Rb—4.16, K—4.32, Na—5.1 volts. These figures may be compared with the following values of ϕ for some solids. (W—4.25, Ta—4.04, Mo—4.04, Na—2.65 volts, Richardson, *loc. cit.*, p. 69).

The chance of success is therefore greatest when one starts with Caesium vapour. Mercury, which has usually been used in these experiments (probably owing to the ease with which it can be handled) is a rather unfortunate choice, for its ionisation potential is very high, *viz.*, 10.40 volts. The permanent gases like H₂ (13.6—17.1 volts), He (25.4 volts), Ne (23.8 volts), O₂ and N₂ would even be still worse.

New light has been thrown on the subject by a series of papers⁴ published elsewhere by one of the authors. In these papers in addition to a formula which enables us to calculate the ionisation of a gas, under different conditions of temperature and pressure, it has been shown that besides the electrical tests, the ionisation can also be detected from a scrutiny of the spectra of the gas.

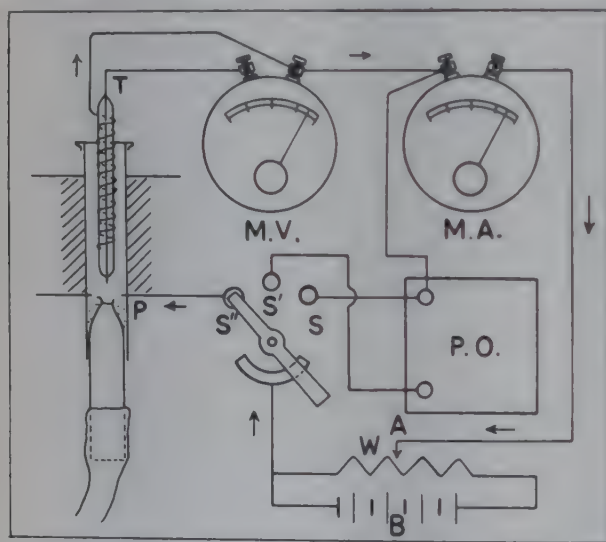
According to these papers, permanent gases first begin to show traces of ionisation only in stars having the highest temperatures (B—stars, having surface temperature of 13000° to 20,000°K) which, it is needless to add, are not reproducible in the Laboratory.

On the other hand, when we apply the same spectroscopic test to the case of the easily ionisable gases Rb, and Cs, we find that they are completely ionised even in the Go class of stars ($T=7000^{\circ}\text{K}$)⁵. In these stars even Potassium is for the most part ionised. According to calculations given in these papers, the heat ionisation of Rb, Cs and K would be appreciable even at temperatures available in the laboratory, and some amount of success may be expected when one tries the experiment with these gases.

These considerations led the authors to choose Cs, Rb and K for the experimental investigation of the effect. But the great chemical activity of these substances was a great hindrance, and after much effort and failure, the experiment reported in the following section was successfully carried out, establishing, probably for the first time, the ionisation of gases by heat.

§ 3. Description of the Apparatus *

After some unsuccessful attempts to measure the conductivity of Cs-vapour contained within an evacuated quartz tube heated by the electric furnace, we adopted the following arrangement. The arrangement may be grasped from the accompanying diagram.



The essential parts consist of the platinum tube furnace P and the thermo-couple T. The platinum tube furnace was vertical and had its lower end closed with a conical-shaped quartz tube having a narrow opening, which was overlayed with a layer of fused pieces of pure magnesia. The quartz tube was connected by a rubber tubing to a hydrogen-generating apparatus. The thermocouple consisted of a capillary porcelain tube of Marquardt mass, carrying a platinum, platinum-rhodium junction.

Hydrogen was allowed to stream through the furnace displacing the air, and the furnace was heated up to 1200°C . Then a piece of Cs, Rb or K, was dropped from a

pincette into the furnace. The metal completely vaporised, and the vapour, on account of its heaviness, displaced hydrogen. Thus we had an atmosphere of Cs-vapour, which was partly ionised owing to the high temperature.

The space within the furnace, containing a fair proportion of free electrons and Cs, may now be compared to an electrolytic cell. The conductivity of the cell was measured by using the walls of the furnace P as one electrode, the pyrometer as the other electrode, according to the ammeter-voltmeter method. The rest of the apparatus easily explains itself.

M. V. is a millivoltmeter (from Siemens & Halske) graduated in temperatures up to 1800°C , for use with the thermo-couple. The graduation was tested anew by a fresh determination of the melting point of sodium chloride.

B is a battery of accumulators, W is an adjustable resistance. By slipping the end A, any voltage could be employed between P and T. M. A. was a millivoltmeter converted into a milliammeter with the aid of a shunt. S, S', S'', are the knobs of a three-way key, P. O. was a post-office box inserted between the two knobs, S, S'. By turning the handle the battery can be put in electrical contact either with S' or S''.

The course of the current while passing through the ionisation space is shown by the arrows. The current was measured by the milliammeter M. A. In this position the post office box is out of the circuit. By simply turning the handle of the key from S'' to S', the cell P, T, is disconnected and the post office box inserted in the circuit. Then proper resistance could be taken out from P, O, till the same deflection, as with the cell, was obtained at M. A. The resistance at P. O. now directly gives the resistance of the ionisation space. The measurement of temperature and the conductivity could not be done at the same moment, because when the space T, P becomes conducting, the voltage from W interferes with the readings of M. V. Hence during the reading of temperature the battery was disconnected. Then the battery was again connected to B, T was disconnected and the deflections in the M. A. observed in the ordinary way.

Hydrogen gas was made anhydrous by passing it through sulphuric acid. The furnace consisted of the platinum tube P, embedded in a concentric porcelain case stuffed with pure magnesia, and was heated by means of a low-tension transformer giving a current of 300 to 1000 amperes under about 2 Volts. The maximum temperature used was about 1200°C . The furnace was the same as that used by Nernst and his students for determining the vapour density of silver.

RESULTS OF THE EXPERIMENT

The conductivities obtained with Es are shown in the Table. Thus the conductivity of the vapour-space becomes almost double when the temperature is raised from 1050°C to 1250°C . It was found that at about 750°C , the conductivity

* The errors in the legends of the diagram have been corrected and duly incorporated.—Ed.

Cs.

Applied Voltage	1	2	3	4	5	
Resistance., T 1050°C	800	700		600	680	mean 736 ohms
at T 1250°C	340	370	360	370	330	mean 354 ohms

could not be measured by the milliammeter, the resistance was >10000 ohms. Owing to the nature of the experiment, the figures are of course rather uncertain, and nothing but qualitative conclusions could be drawn from them. It was also found that the conductivity depended upon the Cs-vapour-content of the cell. When it was driven away by the stream of hydrogen vapour, no trace of conductivity could be found. It is noteworthy that no trace of a saturation voltage could be found. The current increased proportionately as the voltage was raised from 1 to 6 volts. The same experiments were tried with Rubidium and Potassium. The resistance of the cell was found to be for Rb, 1100 ohms at 1200°C, 2500 ohms at 1050°C, for K, 2000 ohms at 1200°C, about 5000 ohms at 1050°C. The influence of the ionisation-potential is quite evident.

Measurements of conductivity at higher temperatures were not tried, because previous experience had shown that above 1200°C platinum becomes plastic and liable to sudden breakage. Theoretical calculations show that at 1800°A, specific resistance of Caesium vapour may be as low as 1 to 2 volts, and by varying the temperature all grades of conductivity between the metallic state [10^{-6} (ohm) $^{-1}$] and the most perfect insulators [10^{15} (ohm) $^{-1}$] can be obtained in the vapours of alkali metals. The experimental difficulties are however formidable. The Drude-Thompson theory of metallic conduction by free electrons, however, fails to lead to any satisfactory agreement. This question will be treated on a later occasion.

§ 4.

We have now to meet the objections which may probably be raised against our contention that the observed conductivity was due to the ionisation of Cs, Rb, and K vapour by heat.

Firstly, it may be argued that the conductivity arises from the surface of the platinum tube emitting thermo-electrons. This explanation is not possible because at the temperature applied by us, the conductivity with a pure hydrogen atmosphere was so small that it could not be detected by the arrangement. This is in accord with the experiments of H. A. Wilson.⁶ The space P. T. became conducting only when Cs, Rb or K was dropped into it, and vanished as soon as the vapours of these metals were driven away by the stream of the hydrogen gas.

Secondly, it may be supposed that the conducting electrons were produced in a secondary way. The thermo-

electrons from the surface of platinum, though by themselves not numerous enough to produce any sensible conductivity, produced new ions on collision with the metal atoms. This sort of ionisation has now become familiar from the works on ionisation potential by Franck and others. But for this effect the potential imposed must be higher than the ionisation potential of the elements. We worked with voltages from 1 to 6 and the conductivity of the ionisation space was always found to obey Ohm's Law.

Hence it is clear that the electrons emitted from the platinum surface or from the magnesia or the marquardt mass play no part, primary or secondary, in the phenomena observed.

Thirdly, it may be argued that the conducting electrons might have arisen from some sort of chemical action, *e.g.*, the action of Cs on MgO producing caesium oxide and free magnesium and the conducting electrons were those emitted by the caesium oxide.

If these were the cases, the conductivity should remain constant and ought not to vanish with the disappearance of Caesium vapour as mentioned before. In fact after the experiment the magnesia pieces were taken out and found to be quite unchanged. No chemical action is known to take place between Cs and H₂. We have satisfied ourselves that even at the highest temperature employed by us, magnesia continues to be a good insulator.

These considerations coupled with the fact that the conductivities observed with Cs, Rb and K are in the reverse order of their ionisation potential just as we would expect from the theory, lead us to conclude that the conducting free electrons owe their genesis to the ionisation of the atoms of these metals by heat alone.

The work was carried out at the Physical Chemistry laboratory of the Berlin University, and it is our pleasant duty to record here our heart-felt thanks to Prof. W. Nernst for the hospitality of his laboratory and for the extremely valuable suggestions with which he was always ready to make our task lighter. The costs were borne by a grant from the Calcutta University, for which the authors wish to record their thanks to the Hon'ble the Vice-Chancellor and the Syndicate.

REFERENCES.

1. Hittorf, Wied. Aun, Nol. 7, p. 592 (1879).
2. Thompson, Phil. Mag., Vol. X, p. 584 (1905).
3. McLennan, Proc. Phys. Soc. Lond., Dec. 1918.
4. Saha, Proc. Roy. Soc. Lond., Vol. 79, p. 135.
5. This was predicted by the author (see Phil. Mag., Vol. 40, 1920, Elements in the Sun) to account for the absence of Rb, and Cs from the solar spectrum. The lines of Rb have subsequently been detected by Russell in the spot-spectrum where, owing to the low temperature, much of ionised Rb is re-converted to the neutral state. (The Astrophysical Journal, March, 1922, p. 128.)
6. Phil. Trans. A, Vol. 202, p. 243 (1903); Electrical Properties of Flames, p. 16, London (1912).

21. ON THE TEMPERATURE IONIZATION OF ELEMENTS OF THE HIGHER GROUPS IN THE PERIODIC CLASSIFICATION

(*Phil. Mag., Sr. VI, 44, 1128, 1922*)

The theory of the temperature ionization of gases and its application to problems of radiation and astrophysics was given by the present writer in a number of papers published during last year. In these papers the theory was limited to the ionization of gas consisting of atoms of a single kind. Recently E. A. Milne and Henry Norris Russell¹ have extended the theory to mixtures of elements. By a comparison of the sun-spot and the solar spectrum, Russell finds that the predictions of the theory with reference to the relative intensity in the hotter and the cooler spectrum of lines associated with ionized and non-ionized atoms are found to be in general agreement with the facts. Russell has also shown that the temperature of the sun and the sunspot comes out to be much more in accord with the figures obtained from general intensity measurements when mixtures of different elements are considered instead of one single element.

But discrepancies have also been pointed out by Russell, which suggests the need of some modification. The nature of these discrepancies may be grasped from the following.

Let I_1 and I_2 be the ionization-potentials of elements A and B. Then at a definite temperature and pressure the ratio of the degrees of ionization of A and B is given by the equation

$$\log \frac{K_1}{K_2} = \log \left(\frac{x_1}{1-x_1} \right) - \log \left(\frac{x_2}{1-x_2} \right) = 5036 \frac{I_1 - I_2}{T}$$

where x_1, x_2 are the fractions ionized, I_1, I_2 are expressed in volts.

If $I_1 = I_2$, x_1 should equal x_2 .

That this is not the case is shown from the fact that sodium and barium have got practically the same ionization potential (5.11 and 5.12 volts respectively), yet both in the sun and in the sun-spot, barium is a good deal more ionized than sodium. The resonance line of Ba, $\lambda = 5535.93$, is absent or very faint both in the solar and the spot spectrum, and it is represented only by the enhanced lines (Ba⁺, $\lambda = 4934.07, 4554.04$), which shows that barium is completely ionized not only in the sun but also in the spot. The resonance lines of sodium, $\lambda = 5889.97, 5895.94$, on the other hand, are very prominent in the

solar spectrum, and are greatly intensified in the spot, which shows that in the sun a large percentage of sodium is unionized, and in the spot the percentage increases owing to a lowering of temperature.

What has been said of sodium and barium admits of a widegoing generalisation, viz. the alkaline earths are, as a rule, much more strongly ionized than their ionization potential would indicate. The behaviour of the alkalis is normal, and we shall see later on that, as a rule, *elements belonging to the higher groups are more easily ionized than elements of the preceding group, and the successive steps of ionization follow each other in rather quick succession.*

First of all, let us consider the relative intensities of the lines of alkalis and the alkaline earths in the sun and the spot spectra.

	Alkalies				Alkaline Earths.		
	I.P. volts.	Intensity Sun	Spot		I.P. volts.	Intensity Sun	Spot
Na	5.11	30	60	Mg	7.65	30	30 ²
K	4.32	6	15	Ca	6.08	20	25
R	4.16	—	1	Sr	5.67	1	3
Cs	3.81	—	?	Ba	5.12	—	—

The table shows that Ba is at least as highly ionized as Rb, though $I_1 - I_2 = 0.96$ volt. Sr is only slightly less ionized than Rb, both in the sun and the spot. Calcium is less ionized than potassium. When we compare the intensity of the lines of Ca, and Na, we find that in the sun they are almost equally ionized (calcium a bit more), but in the spot the recombination between Ca⁺ and (*e*) is much less marked than between Na⁺ and *e*.

Prof. Russell suggests that if the effect of radiation could be taken into account, the theory would be more improved, and the discrepancies could be explained. (See Russell, *The Astro. Journ.*, May 1922).

II

It cannot be denied that the theory is always to be regarded as incomplete until the effect of the general field

¹ Milne, *The Observatory*, Sept. 1921; Russell, *The Astrophysical Journal*, March 1922.

² Russell, loc. cit. p. 130; the intensity given against Mg is that due to the 2p-3s line; the resonance line of Mg, $\lambda = 2852$, is beyond the range.

of radiation can be taken into account. But it is doubtful if this alone will explain all the discrepancies. Another factor, the consideration of which is presented below, seems to play a rather important part.

It is now well accepted that elements of the first group, Li, Na, K, Rb, Cs, have only one electron in the outermost ring, while metals of the second group, Mg, Ca, Ba, Sr, have two electrons in the outer ring. Besides, these two electrons are equally situated—in other words, whenever a Ca-atom is subjected to the action of any physical agency tending to tear off the electrons, it will act equally on both of the valency electrons. In the case of the alkalis, it will act on one electron³ only. Let us take the case of electrolytic solutions. Here the electrical forces act *equally strongly from all directions*, and a calcium atom loses both electrons. The inner electrons being more solidly fixed to the nucleus do not get detached. A sodium atom, on the other hand, loses under the same conditions only one electron, because there is only one electron which can be torn off by the same agency from a Na-atom.

This proves that in the normal case both the valency electrons in Ca occupy nearly identical positions in the atomic system—they are contained in the same part of the atomic volume, and are fixed to the system with forces which are either identical or very nearly identical.

Let us now consider what will take place when a Na-atom and a Ca-atom are subjected to the same ionizing agencies, say bombarding electrons, light pulses, or thermal collisions. For the sake of simplicity we consider the first case only. We shoot at a Ca- and at a Na-atom with the same number of electrons, which are possessed of such energy that they can tear off just one outer electron when it hits at the right place in the atom. Now, assuming the atomic volumes to be the same and the I.P. to be the same, it is clear that the number of successful hits on a Ca-atom will be twice as great as the number of successful hits on a Na-atom for in the outer volume calcium has two electrons, while sodium has only one. In other words, for the same strength of the ionizing agent, Ca-gas will be, roughly speaking, twice as highly ionized as Na-gas.

These considerations may be extended to all cases where ionization takes place by encounter, either with a light pulse or another atom.

In support of this view, an interesting observation by Millikan⁴ may be cited here. Helium has two electrons which, according to Bohr and Lande⁵, are both in the same part of the atomic volume. Millikan finds that when helium gas is bombarded by α -particles, then in one case out of seven, both electrons are simultaneously carried off by the α -particle. This could not take place if one electron

was much nearer the nucleus than the other, and was attached to the nucleus with a greater force. If they are contained in the same part of the atomic volume, then according to the laws of probability, in one case out of eight both electrons would come simultaneously in the same octant, and both would be carried by an α -particle which chanced to pass close to them.

The alkaline earths resemble helium is so far that they have two valency electrons in the same part of the atomic volume in the outermost region of the atom⁶.

In solutions we have always Ca^{++} -atoms and never Ca^{+} -atoms, because the electric forces act equally strongly from all directions. In the cases considered by us, Ca^{+} -atoms are more probable than Ca^{++} -atoms, because the ionizing agencies act from one side only.

The cases of recombination of Ca^{+} and e , Na^{+} and e may be considered in the same light, and we find that in the case of Ca^{+} and e , recombination is more difficult than between Na^{+} and e . If we consider an Na^{+} atom, we find that there are no electrons in the outermost ring, and the positive lines of force proceeding from the nucleus act equally strongly within the 4π solid angles about the atom. From whichever side the electron may approach the Na^{+} -atom, provided other things (energy, distance) are of the right order, the electron will be captured by Na^{+} . Not so in the case of Ca^{+} . It has still got a valency electron in the outermost rings; lines of force proceeding from the nucleus are strongly concentrated on it. In other words, to use the language of Stark, there is a negative patch on one side. An electron cannot be captured if it approaches Ca^{+} from this side. It can be captured only when it approaches the Ca^{+} -atom within only a definite fraction $4\pi/n$ of the total solid angle about the Ca-atom, where n is a number > 1 . We may call ' n ' the "steric factor".

These considerations show that for an atom like Ca, ionization is easier, and recombination of Ca^{+} and e is more difficult than recombination of Na^{+} and e . For trivalent and tetravalent elements like Sc and Si these considerations will apply with even stronger force.

III

It is a more difficult task to take account of the above facts in a statistical theory. To Boltzmann we owe the idea that when two atomic species A and B associate, every case of approach of A and B does not result in a combination, but only when A and B present to each other certain definite parts, $\frac{1}{n_a}, \frac{1}{n_b}$, of their respective surfaces. Boltzmann was of opinion that for the formation of diatomic molecules ' n ' varies directly as the maximum valency of the element (viz. 2 for Ca, 7 for I, and so on)⁷.

³ The strength of the ionizing agent is assumed to be not so large as to be able to tear off any one of the inner electrons.

⁴ Millikan and Wilkins, *Phys. Rev.*, March 1922.

⁵ *Zeitschrift für Physik*, Bd. ix. p. 33.

⁶ It may be pointed out that Langmuir places helium at the head of the alkaline earths (see Loring, "Atomic Theories").

⁷ Boltzmann, *Gasttheorie*, Band ii, pp. 175-177; Jeans, "The Dynamical Theory of Gases," pp. 209-217, 2nd edition.

In recent years the "steric factor" has been introduced into thermodynamics by Stern⁸ in a new theory of the dissociation of I_2 vapour.

Stern considered the case from the standpoint of both thermodynamics and the kinetic theory, and came to the conclusion that ' n ' lay between 6 and 7 in case of combination of two I-atoms to form an I_2 -molecule, thus lending colour to Boltzmann's belief. The kinetic theory is not very convincing, for the following reasons. According to dynamical principles, two particles A and B approaching each other from infinity cannot form a closed system until and unless they lose a certain fraction of their energy, presumably by radiation. Similarly, a molecule AB cannot be dissociated into A and B if the system does not absorb energy from the outside.

Thus a complete theory of ionization is incomplete without a consideration of the mutual action between radiation and matter, and we are beset with the same difficulties which have confronted all investigators on the subject since the days of Boltzmann.

Proceeding to the thermodynamical theory, the fundamental equation was derived from the equation

$$S_a + S_b - S_{ab} = U/T \quad \dots (A)$$

where U =heat evolved, S_a , S_b , S_{ab} were calculated from the quantum theory involving certain assumptions. (Here ' a ' is Ca^+ , b is ' e ', S_{ab} is Ca). The above equations are derived on the assumption that the steric factor $n=1$. Taking the "steric factor" into account, the probability that a and b would simultaneously present the definite portions, $\frac{1}{n_a}$, $\frac{1}{n_b}$, of their surfaces to each other is given by

$$W = \left(\frac{1}{n_a} \cdot \frac{1}{n_b} \right)^n,$$

where N =total number of particles of each species.

The diminution in entropy

$$S_0 = k \ln W = -R \ln (n_a n_b),$$

so that instead of equation (A) we shall have

$$S_a + S_b - S_{ab} - S_0 = \frac{U}{T};$$

hence the equation of ionization takes the form, assuming that only one species of atom is present,

$$\log \frac{x^2}{1-x^2} P = -\frac{U_1}{2 \cdot 3RT} + \frac{5}{2} \log T - 6 \cdot 5 + \log (n_a n_b).$$

The effective ionization potential I_e now becomes

$$U - 2 \cdot 3RT \log (n_a n_b)$$

$$\text{or } I_e = I - \frac{2 \cdot 3RT \log (n_a n_b)}{23000} \text{ volts.}$$

For the electron and the alkalis we can take $n_b=1$. For alkaline earths, if we follow Boltzmann, $n_b=2$, but this

evidently does not suffice in the present case. It may be pointed out that the present case is entirely different from that considered by Boltzmann, for we are considering the combination between an ionized atom and an electron, whereas Boltzmann considered the combination of two atoms. There is no reason why the steric factor should have the same value in both cases.

IV

On the basis of the above formula, let us consider the effective I.P. of helium and the alkaline earths at different temperatures.

Taking $n=2, 4, 6, 8$ respectively, we have for

$$\begin{array}{l} n = 2, I_e = I - 0.060m, \\ \quad = 4, I_e = I - 0.119m, \\ \quad = 6, I_e = I - 0.158m, \\ \quad = 8, I_e = I - 0.180m, \end{array} \left| \begin{array}{l} \text{the temperature being} \\ \text{m-thousands.} \end{array} \right.$$

Russell is inclined to take the temperature of the spot $=4000^\circ K$ and that of photospheric emission $=6000^\circ K$. If this view be correct, the temperature of the spot is only slightly above that of the arc. But we find that in the arc the $Ba \lambda=5535$ is quite strong, while it is entirely absent from the spot. The discrepancy can, of course, be explained by assuming that the temperature of the arc is not uniform; the absorption of $\lambda=5535$ is due to the cooler mantle of gaseous barium next to the air. But more extended research is required to test this point.

Taking the temperature of the spot and the sun to be $5000^\circ K$. and $7000^\circ K$. respectively, and $n=8$, we find that for Ba , $I_e=4.22$ and 3.86 respectively, i.e. in the sun barium is ionized like Cs , in the spot like Rb . This very nearly explains the complete ionization of Ba in the sun, as well as in the spot.

For Ca , $I_e=5.18$ and 4.82 respectively. Thus in the sun, calcium is more ionized than sodium, while in the spot it ought to be a bit less ionized than sodium. This satisfactorily explains the behaviour of the Ca -lines in the sun and spot.

If we turn to the stellar spectra, we find that calcium ' g ' disappears from the B8-stage. By using the original equation of ionization it was found that the temperature could not be less than $13000^\circ K$. But according to Wilsing and Scheiner's intensity measurements, the temperature is only slightly above $10000^\circ K$. Taking $n=8$, the effective I.P. becomes 4.21 volts, the ionization is complete at $10000^\circ K$.⁹ Thus the introduction of the "steric factor" seems to bring down the temperature of different spectral classes in a line with the temperature obtained from intensity measurements.

In my original calculation of the ionization of the helium, the I.P. was taken to be 20.4 volts. This is now known to be

⁸ Stern, *Ann. der. Physik*, vol. xlv.

⁹ Vide M. N. Saha, "Elements in the Sun", *Phil. Mag.*, Dec. 1920.

wrong, for numerous workers have established definitely that real ionization begins at 25.4 volts. The former figures are therefore to be revised. Taking the steric factor =8, the effective I.P. at 25000°K. becomes 21 volts, and ionisation is 74 per cent, under concentrations corresponding to one atmosphere pressure. If $P=10^{-1}$ atm., the ionization becomes complete. Thus the temperature of the Oa stars given in my former paper (Proc. Roy. Soc. Lond, May 1921, p. 151) remains unaltered.

Manganese—Let us next consider the element Manganese, because the constitution of its series spectrum has been recently elucidated by Catalan (Phil. Trans. vol. 223). He finds the 1s term of Mn=59937, the I.P.=7.41 volts. The resonance lines of Mn are the triplet $\lambda=4030.92$, 4033.21, 4034.62, so that, as far as the variation in intensity of its lines in stellar spectra is concerned manganese is an ideal element. According to Lockyer, they occur as faint lines in the spectra of A σ -stars (intensity 1 on a scale 1—10, the Ca-line 4227 being of intensity 2). Thus, in spite of the fact that the I.P. of Mn is 1.23 volts higher than that of calcium, it is more highly ionized at $T=10000^\circ\text{K}$ than calcium. Manganese has got 7 electrons in the outermost shell; its steric factor is therefore expected to be much higher than that of calcium, which probably accounts for its comparatively high degree of ionization.

According to Lockyer, Mn^+ is represented in stellar spectra by $\lambda=4344.19$. It does not occur in King's furnace spectra¹⁰, though groups of lines due to Mn^+ occur about $\lambda=3442\text{--}3497$, 2914-2940. 4344.19 is certainly not a resonance line of Mn^+ . Probably it is of the same type as He^+ 4686. According to Lockyer, this line vanishes from the stage δ Tauri or β Persei. Thus in stellar ranges we have not only Mn and Mn^+ , but Mn^{++} as well. None of the lines of Mn^{++} seems to be known.

Let us now treat some of the other elements in the order in which they occur in the periodic tables. For elements of the third group, e.g. Al, Sc, Y, La neither the series classification nor the variation in intensity of lines in stellar spectra is satisfactorily known. We pass to the next group.

Group IV. Carbon, Silicon, Titanium.

These elements are extremely interesting, because they have got 4-valency electrons, and the steric factor is expected to be unusually large not only for the neutral, but also for the singly- and doubly-charged atoms. As a result, the successive stages of ionization will follow each other in rather quick succession. Unfortunately, the knowledge of the spectra of these elements, as well as of the variation of their intensity in stellar classes, is not so well known.

Carbon—The spectrum of this important element is one of the least known. The line $\lambda=4267$ is supposed to

be due to C^+ ; Lockyer, Baxandall, and Butler¹¹ treat the lines 4650.8, 4647.4 as specially enhanced: we can assume that they are due to C^{++} . One wonders what lines are to be attributed to carbon itself. There are two strong lines, $\lambda=6583.0$, 6577.5 which may be due to carbon. The variation in intensity of the lines of C^+ and C^{++} in stellar spectra is given below:

	A	B9	B6	B5	B3	B2	B1	Bo	Oe5	Oe
$\lambda=4267 (\text{C}^+)$	—	—	2	3	5	5	3	2	—	—
$\lambda=4650.8$ $4647.6 (\text{C}^{++})$	—	—	—	—	1	4	10	25	15	‡

‡ Present, but intensity not exactly measured.

The pair 4550.8 and 4647.6 are very prominent in the spectra of Novae simultaneously with strong enhanced nitrogen lines 4634.34, 4640.82. If the above considerations be correct, carbon occurs in stellar spectra as C^+ and C^{++} , and the two stages follow each other in rather quick succession. This is to be expected of an element having a large "steric factor".

Silicon—Lockyer¹² classified the lines of silicon in four groups, according to their mode of production, and has shown that each group is represented with the greatest intensity in stars at different stages of development. The following is compiled from the Harvard Annals:

	Group I	Group II	Group III	Group IV
Stellar Class.	$\lambda=3905 (\text{Si})$	$\lambda=4131 (\text{Si}^+)$ 4128	$\lambda=4359 (\text{Si}^{++})$ 4553	$\lambda=4089$ 5740
K	?	—	—	—
G	12*	Absent	—	—
F	Present	Present	—	—
A	—	Present	—	—
B9	—	3	—	—
B6	—	3	—	—
B5	—	3	—	—
B3	—	2	1	—
B2	—	1	2	2
B1	—	—	4	5
Bo	—	—	5	15
Oe5	—	—	?	12
Oe	—	—	?	6

* Intensity in the solar spectrum on Rowland's scale.

¹¹ Lockyer, Baxandall, and Butler, Proc. Roy. Soc. Lond. vol. lxxxii p. 352. Fowler, Report on Series in Line Spectra, p. 163.

¹² The Si^+ -pair is present in the star γ Cygni (F8A) and is as strong as in α Cygni (A2F) (Lockyer, Month. Not. R. A. S. 1921). In F5A stars they are weakened, and entirely absent from the solar spectrum. Additional lines of Group IV at $\lambda=5740.2$, 4829.1, 4820.1, 4813.7, have been identified by Fowler in the spectra of β Crucis type B $_0$. Monthly Notices, vol. lxxvi, p. 196.

¹⁰ King, Astro. Journal. vol. liii. (1921).

It is not quite certain if lines belonging to Group III and Group IV can be regarded as due to Si^{++} and Si^{+++} respectively. If Sommerfeld and Kossel's spectral displacement law¹³ be true, the spectrum of Si^{++} ought to have the same constitution as the spectrum of neutral magnesium, i.e. ought to consist of triplets and singlets. Group III and Group IV may be both regarded as due to Si^{++} , Group III belonging to combinations like $1s\text{-}mp_2$, Group IV to stronger combinations like $1s\text{-}mp$. This is of course only a suggestion. But there appears to be but little doubt that in the stellar range available for us, silicon occurs not only as a neutral and a singly-ionized atom, but also at least as a doubly-ionized element, and the stages follow each other in rather quick succession.

Titanium—The spectrum of Ti is very well studied, though the series classification is not yet known. In their general behaviour the lines of Ti, Ti^+ , and Ti^{++} resemble the corresponding lines of Si, Si^+ , Si^{++} , but titanium becomes ionized at a much earlier stage than Si, which is in accordance with the general rule that for elements belonging to the same group, heavier elements have got the smaller I.P. Lines of Ti^+ ($\lambda=3759\cdot47$, $3761\cdot47$, $4578\cdot19$) are quite strong in the solar spectrum, and according to W. J. S. Lockyer¹⁴, they are more intense in F5G stars (ϕ Cassiopeiae) than in A2F stars (α Cygni). The ionization of Ti commences much earlier than that of Si.

Group V. Nitrogen, Phosphorous, Vanadium.

The enhanced lines in the spectrum of Nitrogen and their occurrence in stellar spectra were first noted by Lockyer, Baxandall, and Butler¹⁵. The subject has been subsequently treated by Lunt, Fowler, and Wright.

According to these workers, the spectral lines of nitrogen can be divided into 2 or 3 groups according to the stimulus necessary for exciting them. The chief lines of Group I are $\lambda=3995\cdot15$, $4447\cdot20$, $4630\cdot73$, and the chief lines of Group II are $\lambda=4097\cdot48$, $4103\cdot54$, $4640\cdot82$, $4634\cdot34$. There is, besides, another line at $4379\cdot26$ which seems to belong to an enhanced group of still more pronounced type. Since lines of Group I do not occur in the low-temperature spectral classes like G, F, and even at A0¹⁶, I am inclined to think that they are due to N^+ , or belong to some remote combination of the neutral nitrogen series. In the former case, Group II would correspond to N^{++} . They first come out in the B2 classes (intensity 1), and

gradually increase in intensity as we go to the still hotter stars, as the following shows:-

	29 Canis Majoris (Oe)	Can. Maj. (Oe5)	ϵ Orionis (B1)	β Cen- tauri	γ Orionis
N^{++} (4097.45)	18	6	4	2	1

The lines of N^{++} are very prominent in the spectrum of Novae in their later stages simultaneously with He^+ 4686 and C^{++} 4650.8, 4647.6.

Nitrogen, having 5 electrons in the outer shell, would have a large "steric factor" for not only the neutral atom, but also for N^+ and N^{++} which probably accounts for the quick succession of the different stages of ionization.

According to Lockyer¹⁷, Protovanadium or V^+ , as represented by the line $\lambda=4053\cdot9$, is strongly developed in F5A stars, but shows a weakening in A0-stars, and disappears somewhere about the B8-stage. In the stellar ranges we have, therefore, V, V^+ , and V^{++} in rather quick succession.

It will be seen that the above discussion mainly centres round the life-work of the late Sir Norman Lockyer. To him is due not only the idea, but also extended and elaborate studies of the enhanced and super-enhanced lines of elements, and their application to the study of the ordered sequences in stellar spectra. In this connexion, attention may be drawn to the views which he presented in his 'Inorganic Evolution of Elements'. He tried to impress the idea that the enhanced lines are due to some proto-form or fractional part of chemical atoms. But in those days the atom was an 'elastic solid sphere', and his ideas did not find many adherents. The real significance of his works is being realized in these days of the Rutherford-Bohr theory of atomic constitution.

The present paper probably brings out the great importance of these studies to problems of atomic physics. Lockyer's studies have been continued by American and English workers, but the data hitherto available are not sufficient for the purpose. The above discussion, though scrappy, probably points out the direction in which these studies ought to be extended and amplified.

Note added during correction: Since the paper was written, Russell has published a paper in the Astro. Journal, May 1922, where he has modified the view that Ba is absent from the sun. The $1s\text{-}3p$ line of Ba ($\lambda=3071\cdot59$) has been identified with a line of intensity 00, the resonance line $\lambda=5535$ being probably masked by an iron-line at $\lambda=5535\cdot68$.

¹⁷ Proc. Roy. Soc. Lond. vol. lxiv. p. 396; Phil. Trans. "On the spectrum of α Cygnus," 1903.

¹³ Sommerfeld, *Atombau*.

¹⁴ W. J. S. Lockyer, *loc. cit.*

¹⁵ Lockyer and others, Proc. Roy. Soc. Lond. A. vol. clxxxii, p. 532; Lunt, Monthly Notices, lxxx, p. 534 (1920); Fowler, Monthly Notices, lxxx, p. 693.

¹⁶ Of this last I am not quite sure.

22. ON THE PHYSICAL PROPERTIES OF ELEMENTS AT HIGH TEMPERATURES*

(*Phil. Mag., Sr. VI*, **46**, 534, 1923)

The investigation of the physical properties of elements at high temperature is at present exciting a considerable amount of interest, on the theoretical as well as on the practical side. The present paper is the outcome of certain investigations undertaken by the author, which were withheld from publication because no positive result was obtained. But in view of the recent works, it appeared advisable to give publicity at least to certain points which appear to have been rather lightly passed over by recent workers.

Let us picture to ourselves a quantity of gas, elementary or compound, which is being raised to higher and higher temperatures. The physical changes occurring in the mass under such an increasing stimulus have been discussed in previous papers¹. It has been shown that the gas will become luminous, will emit its characteristic lines—principal lines, sharp and diffuse lines, Bergmann lines—and ultimately will be ionized. The problem before us is: (1) to determine the statistical distribution of the atoms in the various quantum orbits, and from this to deduce the intensity of the different lines of the characteristic spectrum; (2) to determine the electrical and optical properties of such a mass of ionized gas.

The method which the present writer followed was purely thermodynamical. It consisted in the application of a form of the law of reaction-isochore, which was originally developed by Nernst for the study of the dissociation-equilibria of gaseous compounds from their physical properties, to the problem of ionization. The same method was followed in the extension of the method to mixtures of different elements by H. N. Russell². But in this, as in other cases, thermodynamics lead us rather blindfolded to the goal, and do not enable us to see the details of the intervening stages.

A very powerful method has recently been developed by Messrs. Darwin and Fowler³ in a number of important papers published in the *Phil. Mag.* and *Proc. of the Camb. Phil. Soc.* Probably with the aid of this method the problem is brought much nearer to solution, but it seems that there

are a number of important points on which the authors have not laid sufficient stress. The first point to which I wish to call attention is that “no theory of dissociation-equilibrium can be said to be complete unless it takes account of the mutual interaction between matter (atoms) and radiant energy, because at high temperatures, exchange of energy takes place mainly by radiation, and only to a slight extent by collision.”

Binding of an Electron with a Proton (H⁺).

To make the above point clear, we shall consider the simplest case conceivable—namely, the binding of an electron with a proton to form an H-atom. This case can rightly be called the simplest, because, thanks to the Bohr theory, all the possible states of combination are known, and the dynamics can be handled with easy mathematics—advantages which are not present in such cases as the reactions



Let us first treat the dynamical part. An electron starts from infinity with velocity v and passes past a stationary proton. What are the conditions that this will be captured by the proton? A little consideration will show that as long as the energy of the system remains conserved, the electron will describe an hyperbola with the proton as the inner focus, and thus, after wheeling round the proton, will pass off to infinity. In other words, it can never be captured by the proton and lodged in one of the stationary Bohr orbits (having the energy $-\frac{Nh}{n^2}$) unless the system loses the energy

$$\frac{1}{2}mv^2 + \frac{Nh}{n^2} \text{ presumably by radiation.}$$

From physical ground, it seems to be fairly well established that such a process actually takes place in nature in all cases of ionization, giving rise to a continuous spectrum beginning from the limit of the series lines. In the case of hydrogen, the continuous spectrum was first detected by Huggins during the observation of the eclipse spectra, and was confirmed by Evershed. The explanation cited above is due to Bohr. (See ‘*Atombau und Spektralanalyse*,’ p. 547, 3rd edition).

But the dynamical interpretation of this process from the standpoint of quantum mechanics is far from satisfactory, as

* Communicated by the Author.

¹ M. N. Saha, *Proc. Roy. Soc. Lond.* May 1921; *Phil. Mag.* vol. xli. p. 267 *et seq.*, see particularly p. 274.

² Russell, *The Astrophysical Journal*, vol. lv. p. 143; Milne, *The Observatory*, vol. xlv, Sept. 1921.

³ Darwin & Fowler, *Phil. Mag.* vols. xlv. & xlv. *Proc. Camb. Phil. Soc.* vol. xxi. parts 3 & 4.

has been pointed out by Nicholson⁴ in a recent paper. Eddington⁵ has thrown out the suggestion that during its orbital motion the electron loses energy by radiation just as an accelerated electron would do according to the classical theory. But here we are treading on rather dangerous ground, as the satisfactory working out of the suggestion means nothing less than the discovery of the linkage between the classical theory and the quantum theory.

In the case of hydrogen, the continuous spectrum has been observed at the limiting frequency of the Balmer series (quantum orbit 2, or 2_2), but this is owing to the fact that observations do not probably extend up to the limit of the Lyman series. In the case of the alkali elements, the continuous spectrum has been observed extending towards the short wave-length side from the limiting frequency of the principal series. These facts are very decisive in favour of the view that combination of an ionized atom with an electron is always accompanied by liberation of energy in the form of continuous waves of light.

The Statistical part; deduction of the Law of Reaction-isochore for the Ionization of the H-atom.

This part has been worked out by Fowler, but before taking up his method of deduction, I shall give another deduction based on the older methods, because this may serve to bring out the details of the case in a more intelligible manner.

The problem which we are discussing is only a special case of the general problem of association of particles and dissociation of compound particles which was first treated from the standpoint of the kinetic theory by Boltzmann, Natanson, and J. J. Thomson about thirty years ago. A masterly discussion is given in Jeans' 'Dynamical Theory of Gases', p. 213 *et seq.*, 3rd edition. This treatment is applicable, of course with some alteration, to the combination of protons and electrons.

Suppose we have a system consisting of $2v_1$ particles of type A, and v_2 particles of type A_2 formed by the combination of two particles A. Let $v=2(v_1+v_2)$: i.e., v is the total number of particles if there be no aggregation at all.

Then Jeans shows that an encounter between two particles of type A can never result in an association unless the quantity $\frac{1}{2}mv^2+2\psi$ (where 2ψ =mutual potential energy of the particles, v relative velocity of the two particles) assumes a negative value. According to Jeans, "this might be effected by collision with a third molecule [it is not at all clear how], or possibly, if $\frac{1}{2}mv^2+2\psi$ were small at the beginning of the encounter, sufficient energy might be dissipated by radiation for $\frac{1}{2}mv^2+2\psi$ to become negative before the termination of the encounter."

Jeans continues: "we may leave the consideration of this second possibility on one side for the present, with the remark that if this were the primary cause of aggregation, we should no longer be able to use the equations with which we have been working, since they rest upon the assumption of conservation of energy."

The simplest illustration of association is the binding of a proton (H^+) with an electron. As has been already shown, here it is not possible to leave on one side the action of radiation, for that will be tantamount to staging the play of Hamlet without Hamlet's part: for physical evidences decisively prove that radiation is emitted in all cases of the binding of an ionized atom with the electron. Similarly, absorption of radiation is essential for the splitting up of an atom M into M^+ and e .

In spite of rather uncertain knowledge regarding the role of radiant energy in these processes, Boltzmann deduced a formula on the assumption that potential energy exists between two molecules (here we should say between H^+ and e), when the centre of the second (e) lies within a sensitive region surrounding the first (H^+). With this assumption, Boltzmann obtains a formula (formula 503 of page 199, 3rd edition, Jeans's 'Dynamical Theory of Gases') which, with a slight change in notation, can be put in the form

$$\frac{x^2}{1-x^2} P = \frac{kT}{4w} e^{-\frac{U}{RT}} \quad \dots \quad (A)$$

where w =volume of the sensitive region.

Comparing this with the formula for reaction-isobar derived by me, viz.

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\}, \quad (B)$$

we find that

$$w = \frac{1}{4} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \quad \dots \quad (C)$$

or r , the radius of the sensitive layer,

$$r = \left(\frac{3}{16\pi} \right)^{1/3} \left(\frac{h^2}{2\pi m k T} \right)^{1/2};$$

i.e., the radius of the sensitive layer varies as

$$\frac{2.95 \times 10^{-6}}{T^{1/2}} \text{ cm.}$$

Fowler's work on the Reaction-isobar of the Ionization of the H-atom.

We now turn to the very interesting and novel method of deriving the law of reaction-isochore by Messrs. Darwin and Fowler. Fowler deduced the law

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} + B(T), \quad (D)$$

which differs from my formula in the term $B(T)$.

⁴ Nicholson, Phil. Mag. vol. xlv. p. 193 (1922).

⁵ Eddington, Monthly Notices R. A. S. vol. lxxxiii. p. 43.

In the thermodynamical way of derivation of the reaction-isochore the roll of radiation is left obscure. The same remark may be applied to Fowler's method of deduction, as has been admitted by Fowler in the following passage (page 13, Phil. Mag., Jan. 1923):—

"In conclusion, a possible objection may be raised to all the reasoning on which these results are based—namely, that it ignores radiation, whereas in fact a change of quantum state in the molecule probably seldom or never occurs without the emission or absorption of the appropriate radiation."

I would like to add to this passage: Likewise ionization of the H-atom, or association of the proton (H^+) and the electron, seldom or never occurs without the absorption or emission of the appropriate radiation.

Fowler continues: "It is, however, perfectly possible to include the temperature radiation in the statistical discussion, as has been shown elsewhere."

In the passage referred to above (Proc. Camb. Phil. Soc. vol. xxi. p. 263), Messrs. Darwin and Fowler, starting from the partition-function of a Planck line-vibrator, have given an interesting method of deduction of the laws of black-body radiation; but I find it difficult to agree with the view that this includes the temperature radiation in the statistical discussion. They have treated radiant energy as the energy of a single system, the æther, and neglected matter altogether, except through that somewhat shadowy medium, the Planck line-vibrator. But the problem before us is to find out the exact nature of exchanges between Bohr vibrators and radiant energy which has not been covered in the above treatment.

We now come to the consideration of the term $B(T)$ in Fowler's formula.

The term $B(T)$ represents the energy distribution amongst the Bohr vibrators, and is simply another form of the partition function for the internal energy of the Bohr atom. According to Fowler this partition function $b(\theta)$ is given by

$$b(\theta) = \sum_{n=1}^{\infty} n(n+1)\theta^X \left(1 - \frac{1}{n^2}\right)$$

[equation 7·22, p. 20, Phil. Mag., Jan. 1923],

where

$$\theta = e^{-\frac{1}{K\Gamma}}, \quad X = Nh, \quad N = \text{Rydberg number.}$$

As Fowler himself points out, this is a divergent series, and cannot therefore be regarded as solution of the problem. But his suggestion, that the series ought to be cut down to a finite number of terms because the higher terms correspond to orbits with large radii, does not seem to lead out of the difficulty, as imagined by him. For whatever may be the origin of the higher Balmer lines, they are not unknown, nor do they require very special physical conditions for their development. For example, Mitchell could

detect 35 lines of the Balmer series within the lower 2000 kms. of the solar chromosphere, and Wood has recorded 21 of them in his vacuum tubes. The difficulties of dealing with the higher orbits on the quantum conditions

$$\oint p \delta q = nh$$

also been emphasized by Nicholson.

To me, the divergence of Fowler's formula (7·22) appears to be a clear indication that Bohr's hypothesis regarding the weight factor of the higher quantum orbits, viz. $p_n = n(n+1)$, is wrong. In fact, any consideration⁶ which tends to assign to the larger quantum orbits larger probability seems to be opposed to physical facts.⁷

Electrical and Optical Properties of Ionized Gases.

A mass of gas at ordinary temperatures, and not subjected to ultra-violet light, Röntgen light, or any other familiar ionizing agent, possesses no electrical conductivity, because there are no free carriers of electricity present. But if the gas be raised to a high temperature and partially ionized, it will acquire considerable conductivity.

This was pointed out by me in previous papers⁸, and the non-success of previous experiments, as those of J. J. Thomson and McLennan, on the electrical conductivity of mercury vapour were discussed in detail. It was shown that these investigators chose a substance which has too high an ionization-potential (10·45 volts), and hence at the temperature employed by them the mass of gas (mercury-vapour) remained practically unionized.

Caesium is the element having the lowest ionization-potential, and hence I pointed out that this is the element with which success can be expected at temperatures available in the laboratory. Some preliminary experiments undertaken by me at Prof. Nernst's laboratory at Berlin confirmed these expectations. At 1250°C., Cs-vapour was found to have a specific resistance of only 50 ohms, which increased to about 100 ohms when the temperature was lowered to 1050°C. The current could be measured with a milliammeter with a voltage difference of 1 to 2 volts across the ionization-cell containing Cs-vapour, and obeyed Ohm's law throughout the range 1 to 6 volts. These figures are very rough, but they, taken along with the figures for Rb and K (which were found to have increasingly higher resistance), completely confirm the view that the ionization potential is the deciding factor in determining the electrical conductivity of heated vapours.

But great difficulty was encountered when I tried to calculate the conductivity from the Drude-Thomson theory. It was felt that if this theory were applicable to

⁶ For example, Planck, *Berl. Sitzungsberichte*, p. 407, 1915.

⁷ M. N. Saha, Phil. Mag. vol. xli. p. 274.

⁸ "On the Ionization of Gases by Heat," by M. N. Saha and P. Gunther, Journ. Dept. Sci., Calcutta University, vol. iv. See also A. A. Noyes and H. A. Wilson, *Ast. Journ.* vol. lvi. p. 21.

any case, it was the present one. But calculations have not answered to this expectation.

Suppose we have a mass of vapour, say of Cs, which is ionized by heat. Let n_1 denote the number of free electrons or Cs⁺-ions per unit volume, λ_1 and λ_2 the mean free paths, u_1 and u_2 the average velocities of the electrons and the positively-charged particles respectively. Then, according to the Drude-Thomson theory, the conductivity

$$\sigma = \frac{n_1 e^2}{6kT} (\lambda_1 u_1 + \lambda_2 u_2). \quad \dots \quad (E)$$

According to the kinetic theory of gases, if we have a mixture of gases of different kinds (1, 2, ... r , s , ...), then the mean free path λ_r of any particular type r is given by the expression

$$\frac{1}{\pi \lambda_r} = \sum_{s=1}^{\infty} \frac{A_s^2}{r_s} \sqrt{1 + \frac{m_r}{m_s}} \quad \dots \quad (F)$$

[see Jeans, 'On the Dynamical Theory of Gases,' p. 268], where $A_{rs} = A_r + A_s$; the sum of the radii of the " r " and " s " particles, n_s is the concentration of the " s " particle.

In the present case we have to deal with Cs, Cs⁺, and e^- , Cs-particles of course including different types distinguished by the quantum orbits (n_k). Let us neglect all the higher orbits and retain only the fundamental orbit (1_1), a step which will not be acceptable to many, but which is difficult to avoid or improve under the present state of our knowledge.

Then

$$\frac{1}{\pi \lambda_1} = n \frac{A^2}{4}, \quad \frac{1}{\pi \lambda_2} = n A^2 \sqrt{2}, \quad \frac{1}{\pi \lambda} = n A^2 \sqrt{2}.$$

Assuming that the degree of ionization is small (i.e., n_1 is small compared with n , the concentration of Cs-atoms), A denotes the radius of Cs-atom, then $\lambda_1 = 4\sqrt{2}A$ (a well-known result) and

$$\lambda_2 = \lambda, \quad u_1 = \sqrt{\frac{3kT}{m}}, \quad u_2 = \sqrt{\frac{3kT}{M}}.$$

Since Cs⁺ is $1836 \times A$ (atomic weight) times heavier than m , we see that u_2 is negligible compared with u_1 . This only means that the conductivity is mainly due to electrons.

We have now

$$\sigma = \frac{2\pi e^2}{\sqrt{3mkT}} \frac{1}{A^2} x, \quad \dots \quad (E')$$

where x = fraction ionized.

Now " x " can be calculated from the formula of reaction-isochores.

$$\text{We have} \quad \frac{x^2 P}{1-x^2} = \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} T^{5/2} e^{-\frac{U}{RT}}. \quad (B')$$

and

$$P = n(1+x)kT,$$

$$\text{or} \quad \frac{x^2}{1-x} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{1}{n} e^{-\frac{U}{RT}} = \frac{B}{n}; \quad (B'')$$

therefore

$$x = \sqrt{\frac{B}{n}}, \quad \text{or} \quad \frac{B+n}{B+2n},$$

according as " n " is large, or "small" compared with " B ."

The second case will never arise, unless we have to deal with a case of very high temperature and very low pressure (e.g., in the giant stars).

Hence the conductivity

$$\sigma = \frac{(2\pi)^{7/4}}{\sqrt{3}} \frac{(mkT)^{1/4}}{h^{3/2}} e^2 \exp\left(-\frac{U}{2RT}\right) \frac{1}{\sqrt{n}}. \quad (E'')$$

The only thing to notice about this complicated expression is that σ varies inversely as $\sqrt{\text{concentration}}$.

This is an unexpected result, and is not corroborated by my experiments, for I found that the conductivity diminishes gradually as the vapour-content diminishes. *A priori*, it seems rather paradoxical that the conductivity will vary as $1/\sqrt{n}$.

Therefore, either we cannot calculate the percentage of ionization from the law of reaction-isobar at very low concentrations, or the Drude-Thomson theory of conduction which makes the conductivity proportional to the percentage of ionization, and not to the total number of ionized particles present, fails to give us a true picture of the phenomena.

The Mean Free Path of an Electron in a mass of Ionized Gas.

The cause of this failure is not far to seek. We have to calculate the "free life" of an electron in a mass containing normal atoms of Cs, atoms with higher quantum orbits, and Cs⁺-particles. The mean free path, as deduced in formula (F), is based upon the idea of elastic collisions, which is rather the opposite of what actually takes place. As has been explained in the previous sections, in representing the complicated reactions which occur when a free electron encounters a Cs⁺-atom, or a Cs-atom in normal or higher orbits, the idea of elastic collision is of no avail, the exchanges of energy through radiation must be taken into account.

The same considerations apply to the optical properties of ionized gases discussed by Prof. J. Q. Stewart in a letter to 'Nature,' Feb. 10, 1921, but the discussion is deferred to a future date.

[Note: Since the above paper was written, I have been made acquainted, through the courtesy of Messrs. Fowler and Darwin, with a paper by them "On the Intensities of Absorption Lines in Stellar Spectra, etc.," published in the M. N. R. A. S. vol. lxxxiii. p. 403. In this paper Fowler and Milne have given an interesting method of deducing the pressure in the reversing layer by applying a theory of maximum intensities of subordinate lines which they have worked out. It must be admitted that the idea is pregnant with great possibilities, and would lead to important results if the correct partition function $b(\theta)$ can be discovered. But Fowler and Milne have used the function $b(\theta)$ mentioned above, which, being a divergent series, is rather unconvincing.—M. N. S.]

23. ON CONTINUOUS RADIATION FROM THE SUN

(*Nature*, **112**, 282, 1923)

PROF. J. Q. STEWART recently published in these columns (*NATURE*, February 10, p. 186) a very interesting communication on the optical and electrical properties of ionised gases. For some time past I have been engaged in investigations on similar lines, and I wish to direct attention to one important side-result. It is well known that in estimating the surface temperature of heavenly bodies (as has been done by Coblentz, Abbot, Wilsing and Scheiner and others), from their continuous spectra, it is always tacitly assumed that they radiate like perfectly black bodies. Several investigators have pointed out that this assumption does not tally with experimental results. The temperature obtained by applying the total radiation law and the method of isochromatics to the spectral-energy curve are at variance with each other. They are also different from the temperatures obtained from the ionisation theory.

The best example is afforded by the sun, which, according to the careful measurements of Abbot and Wilsing, shows a spectral-energy curve considerably deviating from that of a black body (see E. A. Milne, *Phil. Trans.* vol. 223, p. 218); the fact has been discussed by many investigators, including Schwarzschild, Groot, Milne, Dietzius, and others. There are very weighty reasons why the sun would not radiate like a black body. A black body or a full radiator is one which absorbs all the radiant energy which falls on it, reflecting none. Such an ideal body is nowhere met with in the world, but Wien and Lummer realised it by making use of a hollow enclosure maintained at a constant temperature, and provided with a small hole, the idea being that a beam of radiation within the enclosure would describe an infinitely circuitous path, and what the emission lacks in fullness will be made up by repeated reflections.

It is clear that none of these conditions is fulfilled in

the case of the sun. The surface of the sun contains a large percentage of free electrons, and positive charges, which endow it with a large reflecting power. This point will be clear if we remember the analogous case of metals. According to the electromagnetic theory, metals derive their high reflecting power from the presence in them of a large number of free electrons, or rather electrons which are easily excited to vibration by incident radiation. A theory of emissivity of metals on this basis was worked out by Aschkinass in 1905, and has been verified by the experiments of Rubens and Hagen, Langmuir, and others.

The presence of a large percentage of free electrons on the surface of the sun would, thus, endow it with a high reflecting power. The surface being an open one, the hollow enclosure condition is not realised. Thus the conclusion seems to be irresistible that the total emission from the surface would fall far short of that of full radiator. The form of the spectral-energy curve suggests the emissivity $E\lambda$ varies as $\frac{A}{\lambda^{5+x}}\phi(\lambda\theta)$ where $1 > x \geq \frac{1}{2}$, but about

this point judgment should be reserved now.

Turning to the stars, it is easy to see that similar conditions would hold. The analogy with metals enables us to say that the emission from low temperature stars would fall far short of that from a full radiator at the same temperature, while for stars with very high temperature, emissivity may approach that of a black body.

Prof. Eddington's work on the constitution of stars is based on the assumption that inside the stars total emissivity varies as T^4 ; this assumption is probably not affected, for, inside the stars, the hollow enclosure condition is largely fulfilled.

University College of Science, Calcutta.
July 5.

24. ON AN EXPERIMENTAL TEST OF THERMAL IONISATION OF ELEMENTS

MEGHNAD SARKAR AND NALINIKANTA SIKDOL

(*Ind. Chem. Soc.*, 1, 9, 1924)

Though the theory of thermal ionisation of gases has been given by one of the authors in a number of papers¹ about three years ago, its application has hitherto been confined mostly to the realm of astrophysics. The theory still lacks experimental confirmation in the laboratory, and the present communication is the outcome of an attempt just to remove this desideratum.

The underlying idea may be thus stated:

If we take any element in the vapour state, and go on heating it, its electrical and optical properties will undergo a gradual change. To visualize matters, let us start with Cs-vapour at 800°C. At such a low temperature, it is most probably a non-conductor of electricity and will show only the lines $\lambda=4227$, 1S-2P, $\lambda=6573$, 1S-2 $p_{3/2}$, and other lines of the principal series in absorption. If we go on heating the gas, a stage will come when an appreciable fraction will be ionised. The vapour space will now conduct electricity, and will show the principal lines of Ca, $\lambda=396$ (H), and $\lambda=5933$ (K) in absorption. Between these two stages, the lines of subordinate series of Ca may also come out in absorption.

For sometime past, one of the authors has been trying to follow this process in the laboratory. The first attempt was made with the vapours of the alkali metals, because as these elements possess the lowest ionisation-potentials, it was expected that they would be copiously ionised even at such low temperatures as 800°C-1000°C. But it may be mentioned here that these metals are not suitable for the spectroscopic test, as their chief ionised lines lie far down in the ultraviolet.

The experiments on the electrical conductivity of heated alkali vapours were first undertaken at the laboratory of Prof. Nernst at Berlin, and the preliminary results which we obtained quite confirmed our expectations. It was found that Cs-vapour² at 1250°C possessed an enormous specific conductivity of $(50 \text{ ohm})^{-1}$, which diminished

gradually as the temperature was lowered, and at 850°C. was certainly smaller than $(10000 \text{ ohm})^{-1}$. It was also found that the specific electrical conductivities were in the order Cs > R > K > Na, just as their ionisation-potentials would lead us to expect.

The furnace in which these experiments were carried out was not suitable for continued electrical and optical investigation as described above. Moreover, according to theory, the fraction of atoms ionised is a function of not only the temperature, but also of pressure. Hence it is desirable that a furnace be designed in which both temperature and concentration can be varied at will. In Nernst's furnace, pressure could not be varied at all.

In order to remove these defects, another arrangement was devised, which is described below.

This consists of two furnaces in series. The material which is experimented upon is placed within the small furnace, which is heated to a varying temperature. The vapour pressure of the substance is known from this temperature. The substance in the vapour form is led to the bigger furnace which is maintained at a higher temperature. The volume within the big furnace containing heated vapour forms the experimental space, of which the electrical and spectral properties are studied. The great advantage in this type of furnace is that they allow both the temperature and concentration to be varied at will, which is not possible in the type used by A. S. King at the Mount Wilson Solar Observatory.

THE FURNACE.

The furnace is shown diagrammatically in Fig. 1. It is simply an adaptation of Prof. Chompton's furnace (described in the *Journ. Opt. Soc. America*, Oct., 1922), with some modification to suit our convenience.

B=A rectangular hollow brass base, made of thick sheets of brass cooled by water, by inlet and outlet pipes at P and P'.

T=Heavy box of cast iron in the form of a rectangular parallelepiped, open at the bottom, and provided with flanges on all sides at the bottom for air-tight contact with the brass base. The joint was kept air-tight by a preparation of resin and bee's wax.

¹ *Proc. Roy. Soc. Lond.*, Vol. 99, p. 136, *et seq.*, *Z. f. Physik*, Vol. 6, p. 40.

² Lewis reports in his *Thermodynamics* (p. 460). Urey carried out at his suggestion a similar experiment on the electrical conductivity of heated Cs-vapour. The full details of the paper are not yet available. The experiment mentioned above is fully described in the *Journ. Dept. of Science*, 1922, Calcutta University.

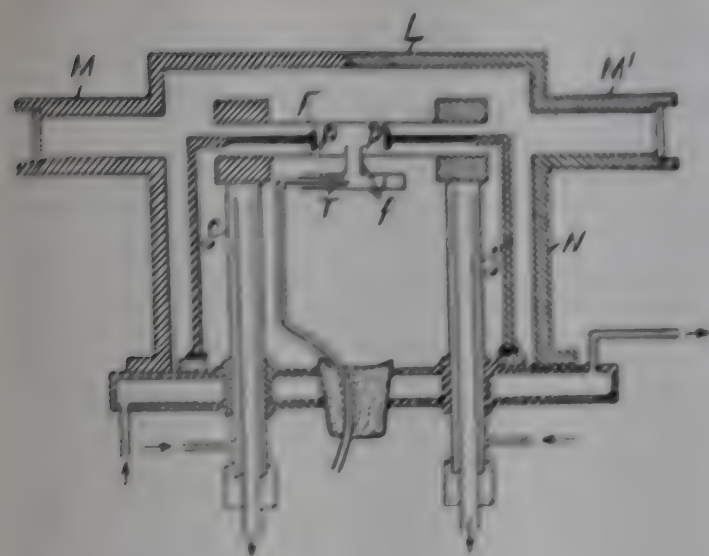


Fig. 1

M, M'—Projecting tubular pieces, of one piece with the box, and closed by glass or quartz plates, which are cemented to it by means of shellac.

L—Removable circular lid with a ground conical periphery and fitting into a ground, and sloping circular opening on the top of T. By taking out L, easy readjustments could be quickly made in the interior. This was just to avoid taking off the whole box T after every experiment for the necessary readjustments. The two surfaces of contact were ground with great care till they fitted exactly into each other.

F—Furnace which in the preliminary experiments consisted of a sheet of iron rolled into the form of a circular tube. It was clamped by means of a lead plate and screws on the water-cooled stands, S and V which consist of thick iron tubes with a rectangular top of solid iron. The stands were water-cooled as shown in the diagram. The surface of the stems was cleaned by the pickling process used in enamelling and then smoothed by emery paper.

D—A thick wire of iron, clamped on the stand S at one end and sliding in a groove at the head of the stand V at the other end.

About half the space inside the furnace F was clear.

A current of 500–1000 amperes was applied to F under 6–10 volts directly from a battery of accumulators with a sliding resistance of mercury. Owing to the large size of the furnace, and the limited energy supply at our disposal, temperature could not be raised higher than 1250° C, as eye observations would indicate. A low tension transformer as used by King would have been much better, but as we had not the means to buy one, we had to make the best use of a set of discarded storage cells. One great disadvantage was that after about 5 minutes the connecting wires became very hot, and less current flowed through F, and temperature rapidly fell. This defect would probably

be cured if the furnace could be heated by current from a low-tension transformer, with very short and water-cooled leads. The furnace was evacuated by a Gaede oil pump, which was kept continuously running during the experiment. The leak was so small, that even at a temperature of 1250°, iron did not appreciably oxidize through the experiment lasted from 5–10 minutes.

f—Another furnace of much smaller dimensions, heated directly by current from accumulators, the substance which was to be vaporized was kept inside the furnace here. The ends were blocked by iron-plugs, through one of which passed a thermocouple of iron and constantan shielded by Pyrex glass tubing.

t—Small porcelain tubing, leading the vapour through an orifice at the top of f to the heated space inside F.

The connections to f for leading the heating current consisted of thick copper rods (not shown in the diagram) passing through an India rubber cork, which closed an orifice at B. The leads for thermocouple were also taken through this cork.

The temperature to which f was heated could be obtained from the readings on the millivoltmeter to which the couple was connected. Then from the data on the variation of vapour pressure with temperature, the pressure in f could be obtained. The pressure in f is equal to that in F, if the free flow could be prevented by stopping the ends of F by quartz plates. This has not yet been attempted.

By this arrangement, it was hoped that the vapour of any element could be maintained at a definite pressure for any length of time. Experimental difficulties have, however, not been completely overcome, but the progress hitherto made has been sufficient to justify the expectations placed in this arrangement.

DESCRIPTION OF THE ARRANGEMENT FOR MEASURING THE ELECTRICAL CONDUCTIVITY.

The arrangement for measuring the electrical conductivity is shown in diagram No. 2.

B—Battery.

V—Voltmeter for measuring the potential difference between the central wire and the furnace.

F—Furnace.

R—Resistance for varying the voltage.

K₁ K₂—Two three-way keys.

M. A—is a milliamperemeter placed between one set of knobs of K₁ and K₂.

Mic. A—is a microampere-meter placed between another set of knobs.

G—is a sensitive galvanometer placed between another set of knobs, with a variable megohm in series. By manipulating the key K₁ K₂ the furnace may be connected either through the milliammeter, the microammeter or

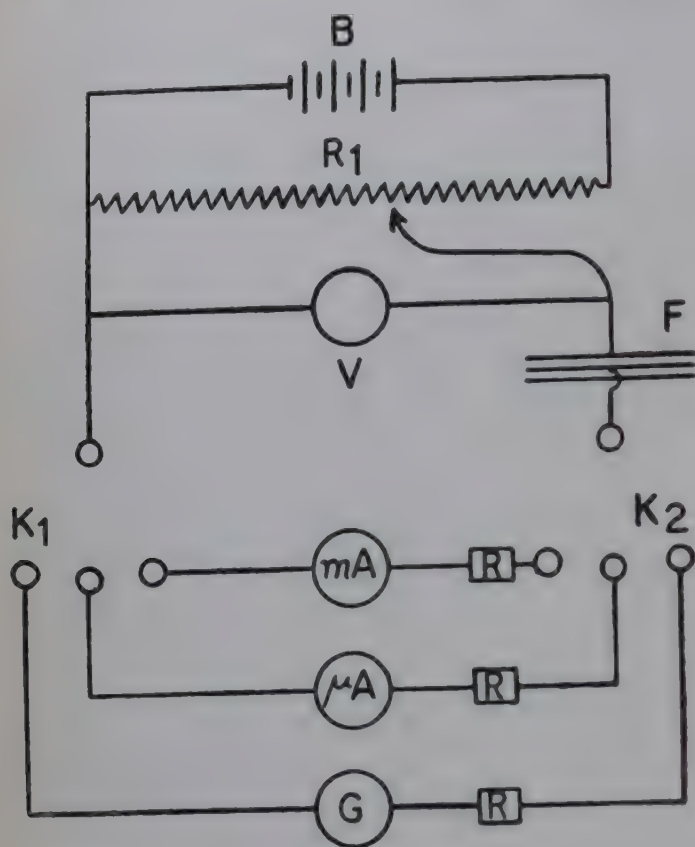


Fig. 2

the galvanometer. Voltage divided by the current gives the resistance of the vapour-space in the furnace.

ACTUAL EXPERIMENT.

The results which are communicated here are only of a preliminary nature.

The actual procedure was as follows:

Firstly, the central furnace was heated, and the thermionic current between the furnace and the central wire was measured. In most cases, this could be done by means of the galvanometer.³ The thermionic current is a very good indication of the temperature of the furnace F. Then current was applied to the small furnace *f*. The substance vaporised, and the vapour passed into F. Then the observer at the galvanometer noted whether the spot of light in the galvanometer scale shifted its position. Simultaneously, another observer noted the readings on the millivoltmeter connected with the thermocouple.

³ It will be interesting in this connection to recall the experiment of Pring and Parker who investigated the thermionic emission from large carbon rods by heating them with the aid of very large currents. They found that with larger currents thermionic emission died down. Richardson pointed out that this was due to the large magnetic field of the heating current, which prevented the electrons to escape from the heated surface. In our experiment though we are using currents of the order of 10^3 Amp. the experiment is being performed *inside* the heated space, where the magnetic field is zero, so there is free thermionic emission. Incidentally, it may be mentioned that in this method the temperature of the emitting surface can be more precisely measured, if we direct the optical pyrometer to the interior, for radiation coming from inside the furnace approximates to the black body condition. The point is receiving attention.

If the spot of light went off the scale, the galvanometer circuit was shunted off, and the microammeter circuit was put in, and the current observed. If this did not suffice, the milliammeter circuit was inserted.

The pump was kept running during the whole course of the experiment, which generally took from 5 to 10 minutes.

When experiment with one substance was finished and the furnace cooled down, the lid was taken off. Then the small furnace *f* was replaced by a fresh one, because the old furnace is generally contaminated by deposits of the metal with which the previous work has been done. The big furnace F was replaced, only if it was broken, as frequently happened, probably owing to stress developed during expansion.

Series 1. Experiments with Hg, Cd and Zn.

These three metals are interesting because the electrical conductivity of their vapours in a flame were investigated by McLennan⁴ a few years ago. The electrical conductivity of heated mercury vapour has formed the subject of investigation by many workers including Maxwell, Hittorff, J. J. Thomson and Strutt, but the results were mutually contradictory. McLennan's results also were quite indecisive.

We have proved decisively that when vapours of these elements are introduced into the furnace, between the temperature 850°C to 1300°C , the thermionic current remains completely unaltered. The voltage applied was 1.34, and at the highest temperature employed by us (1300° as judged by visual observation), the thermionic emission was 10 microamperes, with $R=9000$ ohm in series. The temperature of the small furnace was 650°C , corresponding to a vapour pressure of 27.23 mm, of Zn. It was found that when Zn-vapour was evolved, there was not only no increment in the thermionic current but there was actually a slight falling off, owing probably to the cooling of the furnace by the passing Zn vapour. The same phenomena was observed with Hg and Cd, the last being operated at a temperature of 740°C , vapour pressure = 557.2 mm. of mercury.⁵

These experiments prove conclusively that vapours of Zn, Cd, and Hg are not ionised at all by heat up to temperatures of 1250°C . This is quite expected as the ionisation-potential of these elements are rather high, viz., 9.45, 9.40, 10.45 volts.

Experiments with Mg and Ca.

Magnesium.—The small furnace was heated to 750° (measured), and the large furnace to about 1300°C (not

⁴ Proc. Roy. Soc., Lond., Vol. 92, p. 592.

⁵ These figures are taken from Landolt and Bornstein's Tables, 6th edition, pp. 1332-1338.

measured). The thermionic current was 10×10^{-6} amperes. On putting Mg-vapour, the current rose to $\frac{2}{10}$ of a milliampere, or 200×10^{-6} Amp. or by about 20 times, so that magnesium vapour seems to have been ionised at 1300°C .

Calcium.—The small furnace was maintained at 920°C (measured), but the storage cells having run down, the temperature in the big furnace F could not be increased. It was probably 1150°C . The thermionic emission was less than a microampere, but on putting Ca-vapour, it rose to 30 microamperes. This proves that Ca-vapour is appreciably ionised at 1100°C .

Sodium

Sodium.—The small furnace was maintained at 470°C , corresponding to a vapour pressure of about 2 mm. of mercury. The temperature in the big furnace was about 900°C . The thermionic emission amounted to 40 divisions on the galvanometer scale corresponding to a total resistance 5×10^6 ohms. As one megohm was put in the galvanometer circuit, the resistance of the furnace-cell was approximately 4×10^6 ohms. On putting Na-vapour the spot went off the scale at once, so that the microampere circuit was put in. Even this went off the scale. Then the milliamperemeter circuit was put in with no resistance in series. The current was $\frac{1}{10}$ of a milliampere, so that the

equivalent resistance with Na-vapour was only 13400 ohms. Thus at 900°C the conductivity of the space increases about three hundred times, when Na-vapour is put in.

The only objection which can be raised against the view that Na or Ca-vapour is ionised by heat is that the electrons emitted from the surface of the furnace F in falling to the central wire, produce fresh ions by collision. This possibility is excluded by the fact that the potential difference between the furnace and the central wire is only 1.34 volts, much lower than the ionisation potential of the elements investigated. But it may be contended that since the total potential fall between two ends of the furnace is from 6 to 10 volts, electrons emitted from the negative end may just slip along the surface and come out at the end with an energy corresponding to a voltage drop of 6 to 10.

Though we can think of such an eventuality, the probability of its affecting the main results seems to be rather remote. At least, in future experiments, efforts will be made to free the arrangement from the possibility of such an objection.

In conclusion, we wish to record our thanks to our colleague Mr. S. Bhargava, Reader in this University, for useful help in designing the apparatus and to Mr. K. Majumdar, Research Scholar, for help in taking observations.

25. ON AN ACTIVE MODIFICATION OF NITROGEN*

M. N. SAHA AND N. K. SUR

(*Phil. Mag.*, *Sr. VI*, **48**, 421, 1924)

A few years ago Prof. Strutt (now Lord Rayleigh) performed a series of experiments on an active modification of nitrogen¹, which excited a good deal of interest at the time. Nitrogen is well known to be an extremely inert gas, but Lord Rayleigh showed that if a condensed spark discharge be sent through N_2 -gas, the glow persists in the gas flowing out of the region of the discharge, which shows considerable chemical and spectral activities. The spectrum of the afterglow was investigated by Fowler and Strutt² and shown to consist of the usual α , β , and γ groups of

positive bands, with a fourth group which was observed for the first time.

The object of the present paper is to show that almost the whole series of observations recorded by Lord Rayleigh can be explained on the basis of Klein and Rosseland's theory³ of inelastic collision of the second type, which has been further developed by Franck⁴ and his students. For convenience of discussion we begin with a short account of this theory.

The experiments on ionization potential and origin of

* Communicated by the Authors.

¹ Strutt, *Proc. Roy. Soc. Lond.* lxxxv. p. 219; lxxxvi. pp. 56, 105, 529; lxxxvii. pp. 179, 302, 381; lxxxviii. pp. 110, 539.

² Fowler and Strutt, *Proc. Roy. Soc. Lond.* lxxxvi pp. 105-117.

³ Klein and Rosseland, *Zs. f. Physik*, iv. p. 46.

⁴ Franck, *Zs. f. Physik*, ix. p. 259; xi. p. 155. *Cario*, *Zs. f. Physik*, x. p. 105 and p. 166. *Compton, Journal of the Optical Society of America*, 1923.

spectra, which were first carried out by Franck, are now matters of common knowledge. They deal with the interchange of energy between freely moving electrons and atoms. A stream of electrons moving with a definite velocity is projected into a mass of gaseous atoms. When an electron happens to pass close to an atom, then, provided the energy of the free electron exceeds a certain limit given by the quantum condition $eV = h\nu$, the whole of its energy may be transferred to the valency electrons lying at the outer periphery of the atom. The valency electron is thereby lifted to higher quantum orbits. These states are not stable, and in a short time it reverts to its original position, the excess of energy being set free as monochromatic radiation. Thus the atoms abstract energy from the free electrons, and convert it to energy of its own monochromatic radiation. This process is indicated by kicks in the current-potential curves, as well as by the emission of the characteristic spectrum of the element. When the energy of the bombarding electron is sufficiently large, it may tear off the valency electron from the parent atom. This stage is known as ionization and indicated by an abrupt rise of the current in the current-potential curve.

Hitherto, attention of all workers has been confined to only one side of the problem, *i.e.*, communication of energy by the free electron to the atom. But Klein and Rosseland showed that the reverse process (*viz.*, communication of energy by the excited atom to the free electron) actually takes place in nature on a very large scale, and accounts for a large number of experimental results recorded in previous years. For example, suppose we have a mass of mercury atoms, some of which has been activated either by absorption of the light $\lambda = 2536$ ($1S-2p_2$) or by an electric discharge from the normal ($1S$) stage to the next stage $2p_2$. If, now, an electron passes close to this mercury atom ($2p_2$ stage), what will take place? According to older conceptions, we could think of no other process than that the electron would communicate its energy to the mercury atom, and excite it to still higher quantum states or to ionization. But Klein and Rosseland pointed out that the reverse process may also take place, *viz.*, the mercury atom may transfer its extra amount of energy corresponding to $\lambda = 2536$ to the electron. The electron thus receives an increment in its velocity, but the transfer is "radiationless," *i.e.* the electron *chokes the emission* of the light $\lambda = 2536$, which would have otherwise certainly taken place. The chance of this "radiationless transfer" depends upon circumstances which are yet to be worked out, but there seems to be no doubt that it is a very general phenomenon.⁵

These considerations were further extended by Franck and his students, who showed that the excited atoms may communicate their energy not only to the electron, but also to such atoms or molecules as may come in contact with them. These atoms or molecules will therefore receive either some increment in their kinetic energy or, if the energy imparted be sufficiently large, they may be excited to their spectral emission, ionization or dissociation in the case of molecules.

These ideas, therefore, open up a very promising field of investigation, and Franck has already pointed out, and confirmed several interesting deductions. For example, a stream of mercury gas was excited by $\lambda = 2536$, and these activated Hg atoms were allowed to act upon the H_2 -gas. It was proved that the H_2 -gas was thereby dissociated into atoms. The explanation is that when a mercury atom absorbs the light $\lambda = 2536$, it is loaded to an energy-content of 4.9 volts. On coming into contact with the H_2 -gas it delivers this energy to the molecule of H_2 which is thereby broken up into atoms, as the heat of dissociation corresponds to about 3.8 volts (80000-90000 cal.).

Transference of energy to atoms.

Hg atoms activated by $\lambda = 2536$ were allowed to act upon vapours of thallium and silver. Only such lines of these vapours were excited for which the energy required is less than 4.9 volts.

Choking Effect of Inert Gases on Luminous Mercury Vapour.

Wood⁶ carried out years ago a number of very interesting experiments on the luminescence of mercury vapour excited by an electric discharge. He found that if inert gases like N_2 , He , A were added to the luminous Hg-vapour, the luminosity was quenched, the decrease in luminosity being roughly proportional to the amount of gas added. The explanation according to Franck is as follows:—When an activated Hg atom comes into collision with an atom of A or He , then in some cases energy is communicated to the latter. This results simply in an increase of the kinetic energy of the A or the He atom, as the amount of energy transformed (4.9 volts) is quite insufficient to lift the vibrating electron of A or He to the higher orbit. The net result is, therefore, the quenching of the line $\lambda = 2536$ Å.U. or other lines of the Hg spectrum.

The phenomenon is therefore quite general. If to a mass of luminous gas another gas is added of which the radiation potential is higher than that of the luminous gas, the luminosity is choked.

⁵ It may be noted here that Klein and Rosseland were led to this conception from Einstein's idea of "Negative Einstrahlung" or negative absorption. A Hertzian oscillator when placed in a field of radiation may either take up the energy from the field, or give up its own energy to the field, according as the phase difference between the vibration of the resonator and the incident radiant waves is less or greater than 90° . The former case is positive absorption, energy being taken up by the

resonator from the field. The latter case is negative absorption, energy being given to the field, just as in alternate current instruments, if the phase difference between the current and potential is $> 90^\circ$, the work done by the instrument $EI \cos \phi$ becomes negative, *i.e.*, work has to be done on the instrument.

⁶ Wood, *Phys. Zs.* xiii. p. 353 (1912).

To those who have followed the work of Lord Rayleigh on active nitrogen, the foregoing discussion would seem to hold out promises of a very satisfactory explanation. But all is not plane sailing as the following discussion will show. We begin with a concise statement of our explanation.

When a moderately condensed discharge is sent through N_2 -vapour it is converted into an excited state, falling just short of dissociation into its constituent atoms. The amount of energy to which the molecule is loaded lies between 8.2 and 8.5 volts. The average life of such an excited atom is of the order of 10^{-8} second. When the excited nitrogen molecule falls back to the original state, it emits a band-spectrum lying between $\lambda=1600$ and $\lambda=1200$.⁷

This band may be called the primary band, and the usual bands lying in the visible region (the positive bands) stand to this in the same relation as the subordinate series of an element stand to the lines of the principal series.

The arguments in favour of this view are as follows:—The spectrum of active nitrogen was investigated by Fowler and Strutt⁸, and found to consist of the α and β groups of positive bands, which according to the canal-ray method of Wien⁹ are due to the N_2 molecule. None of the lines of the familiar line-spectrum (attributed by Fowler to N^+) were observed. (It is still a moot point whether the lines due to N atom, recorded by Stark and Hartdke¹⁰, were present, as the above-mentioned investigations did not extend up to this region). None of the negative bands, which according to Wien are due to N_2^+ , were present.

The evidence is thus fairly conclusive that N_2 -gas in the afterglow region simply consists of excited N_2 molecules. The experiments of Lord Rayleigh¹¹ to detect whether charged particles were present in the afterglow were entirely negative.

It is also clear that the afterglow bands cannot be the primary bands, for unexcited N_2 -gas is completely transparent to this region. It has got an absorption band lying between $\lambda=1600$ Å.U. and $\lambda=1200$ Å.U. That the primary band lies in this region is also proved by the experiments of Brandt¹², who, using the bombarding electron method of Franck, found an abrupt rise of current in the neighbourhood of 8.2 volts. Several kicks were observed in the current-potential curve between 8 and 9 volts, and these were shown by Brandt to be of the nature of band-emission. The primary emission bands therefore lie between $\lambda=1600$ and $\lambda=1200$ Å.U., and are present in the afterglow region. But the glass of the quartz vessels in which these experiments are carried out completely masks them.

The visible bands which are actually observed are simply secondary. Their final orbit is also unstable, just as the

final orbits corresponding to the Balmer-lines of H are the diquantic unstable orbits. These bands will therefore be emitted only when these orbits have a certain amount of stability.

According to this view, active nitrogen simply consists of the excited nitrogen molecule loaded to the energy of about 8.5 volts (corresponding to about 1.9×10^6 calories). Its great activity is due to the ease with which the particle can part with this amount of energy. When foreign atoms or molecules are not present or present only in small amounts, the excited molecule reverts to the normal state after emission of the primary and the secondary (the usual positive) bands. The average life of the excited atom when it suffers no collision is about 10^{-8} sec.¹³, but this may be lengthened when the number of collisions is large. This point will be discussed later on.

When foreign substances are present, the energy is mostly communicated in a radiationless transfer. The foreign substance is thereby stimulated either to luminescence or to chemical activity. The following few selected examples will bring out the point clearly.

(1) Active nitrogen, when passed over sodium, causes not only the D_1 and the D_2 lines, but also the subordinate series lines to flash out.

The amount of energy required for the excitation of the yellow lines is only 2.1 volts, so that the energy delivered by active nitrogen is sufficient, not only for exciting its entire line-spectrum, *but may probably also suffice to ionize it*, as well as the other alkali elements. Lord Rayleigh found that the maximum emission is at the second line of the principal series 3303. This is probably due to the fact that the energy transferred is very large compared with the excitation potential of Na.

(2) Action on mercury.

Active nitrogen, passed over Hg-vapour, excites the fundamental line $\lambda=2536$ ($1S-2p_2$) and lines belonging to the triplet group of the first subordinate and second subordinate series. The $2P-3D$ line ($\lambda=5790$) and $2P-3d'_2$ line ($\lambda=5769$) are not excited, hence probably an upper limit to the energy transferred is obtained by assuming that it just fails to excite the 3D level in the Hg-atom. This is 9.4 volts, which is in accordance with our theory.

(3) Action on magnesium.

Many arc-lines are developed, but neither the line 4481

⁷ Lyman, 'The Spectroscopy of the Ultra-Violet,' p. 63.

⁸ Proc. Roy. Soc. Lond. lxxxvi. pp. 105-117.

⁹ Wien, *Ann. d. Physik*, lxix.

¹⁰ Stark and Hartdke, *Ann. d. Physik*, lvi. p. 303.

¹¹ Strutt, Proc. Roy. Soc. Lond. lxxxviii. p. 183.

¹² Brandt, *Zs. f. Physik*, viii. p. 32.

¹³ Wien's method of determining the charge on luminous atoms may be noted here. He allowed a stream of luminous gas to flow out of a canal-ray tube into a space where a vacuum of the order of 10^{-3} to 10^{-4} mm. is continuously maintained by a number of diffusion pumps. In this space, the gas is allowed to pass between two parallel plates which are maintained at a small distance apart at a constant difference of potential. The spectrum of the luminous slit-like region is photographed. Particles which are uncharged show straight spectral lines, while lines due to charged particles are bent one way or the other. The vacuum in the space is so high that no collision takes place amongst the particles. In this way Wien proved that the β groups of positive bands are due to the uncharged N_2 molecules, whereas the bands in the negative glow are due to N_2^+ molecules.

nor any other spark-line was excited. The arc-line $\lambda=4703$ (1P—4D) was either not excited at all or excited very feebly.

The ionization potential of magnesium is 7.65 volts, and thus active nitrogen would just suffice to ionize magnesium. Active nitrogen passed over Ca, Ba, or Sr, would excite, besides their arc spectrum, also the spark spectrum.

(4) Hydrogen and the inert gases have no other influence on active nitrogen except a mere dilution of the glow. This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active energy.

On the other hand, when helium is activated by an electric discharge, it is capable of storing a large amount of energy ($e=20.4$ volts) and hence would be found to be an extremely active substance. This view is supported by an interesting observation of Lord Rayleigh¹⁴ in a recent paper, who found that activated helium on coming into contact with N_2 -gas (unexcited) excites the afterglow. If the present view is correct, it would excite not only the positive bands but also the line-spectrum due to N. This point ought to be further investigated.

We now come to the most formidable difficulty confronting the above explanation, viz., chemically pure nitrogen shows no afterglow at all. This matter forms the subject matter of a very interesting paper by Lord Rayleigh in vol. xci. of the P. R. S. London. Following experiments by Tiede and Domcke, who found that chemically pure nitrogen, prepared by heating barium and potassium azide, and carefully freed from all impurities, shows no afterglow at all, Lord Rayleigh showed that nitrogen purified by prolonged standing over the liquid alloy of Na and K gave an afterglow, which was however very faint. On introducing small impurities of oxygen, or almost

any easily excitable gas (1 in 1000 parts), the glow was restored to full brilliancy. This observation has also been confirmed by recent experiments of Pirani¹⁵, who claims for his nitrogen a purity of 5×10^{-5} per cent. Pirani finds that perfectly pure N_2 shows no luminescence at all, though admixture of electronegative gases like O_2 , H_2O , I_2 in concentration of 1.5×10^{-3} give a maximum after-luminescence. Large admixtures, say from 6 to 8×10^{-3} , choke the luminescence. In all these experiments, the authors seemed to have looked only for the after-luminescence of the chemically pure gas as a test of activity. They did not evidently apply the chemical tests. This point is of some importance, because the afterglow is simply the sign of the return of the molecule from the higher quantum states to one of the intermediate unstable states; it does not indicate the reversion to the normal state. Hence, if under certain conditions the intermediate orbits (*i.e.* final orbits of the afterglow band) be not stable, these will not be emitted at all, though the gas will exhibit all the chemical and spectral activity recorded by Lord Rayleigh.

It seems to be a general phenomenon that the activated atom, when left to itself, has always a tendency to fall to the lowest quantum state, without stopping at the intermediate stages. Hence only the primary bands would be emitted. This is confirmed by an interesting investigation of Wood¹⁶, who finds that in his discharge-tubes, Balmer lines of H (for which the final orbit is an unstable orbit) are always rendered very brilliant if H_2O vapour is present as an impurity. The subject is, however, well worth further investigation.

Our explanation of the absence of afterglow in active nitrogen, if true, would mean that nitrogen may be loaded to an energy of about 8.5 volts without being luminous, and therefore will still possess all other properties associated with active nitrogen.

¹⁴ Lord Rayleigh, Proc. Roy. Soc. Lond. vol. cii. p. 454.

¹⁵ Pirani, 'Chemical Abstracts,' 1923, ii. p. 157.

¹⁶ Wood, Phil. Mag. xlii. p. 729.

26. THE PRESSURE IN THE REVERSING LAYER OF STARS AND ORIGIN OF CONTINUOUS RADIATION FROM THE SUN

(*Nature*, **114**, 155, 1924)

There seems to be at present a wide divergence of views regarding the magnitude of pressure in the "reversing layers" of stars. While earlier investigators assigned to it a pressure of one to ten atmospheres, on the basis of pressure shift of lines to the red, these experiments do not appear to carry much weight at present. Fowler and Milne (Monthly

Notices R.A.S., vol. 83, p. 415, 1923) actually assign to it a pressure of the order of 10^{-3} to 10^{-4} atmospheres.

The following speculations will show that probably an accurate method of determining the pressure may be developed from the limit of series absorption of elements in the Fraunhofer spectrum. To introduce the subject, let

us start with the well-known fact that in the Fraunhofer spectrum of the sun the Balmer series of H absorption lines abruptly terminate at H ζ , while in the flash spectrum no less than 35 Balmer lines are found. Here the ionisation theory does not help us, for all Balmer lines require the same H atom (in the diquantic state) for absorption. We are therefore confronted with the fact that as continuous radiation pours through the H(2) atoms, pulses which lift the electron up to the 8th quantum orbit are freely absorbed, but pulses which would lift the electron to the higher orbits somehow fail to be absorbed in spite of the presence of suitable absorption centres. Something prevents the development of the H-orbits beyond certain limits.

The next step is naturally to identify this agency with the congestion in the reversing layer due to high concentration of particles. In order that the n th-orbit may be developed, the electron should be capable of passing to an average distance of $0.532 \times 10^{-8} \times n^2$ cm. from the nucleus. But if within this distance it comes under the influence of a second nucleus, or another electron, there can be no free development of the orbit: the electron will become either free, or attach itself to another nucleus. Hence for rays shorter than H ζ , the H(2) atoms in the particular layers treated will lose their power of picking up the pulses corresponding to the Balmer series, but will exercise a sort of general, though much enfeebled, absorption on all radiation beyond H ζ , somewhat after the manner of X-ray absorption. This part will be freely emitted only by higher layers, where the pressure has fallen to sufficiently low values; in other words, if the solar atmosphere were composed of H(2) atoms only, part of the continuous spectrum beyond H ζ would originate from somewhat higher levels than the redder part of the spectrum.

The idea helps us to get a clearer view of the origin of continuous radiation from the sun. For what has been said of H(2), absorption is a general phenomenon, and can be extended to all other elements. In fact a scrutiny of the Fraunhofer spectrum shows that quantum orbits higher than the 5th or the 6th (total quantum number) are rarely developed. The examples given in the following table illustrate the point¹.

For every one of these elements conclusions similar to that in the case of hydrogen hold. Thus, since the higher members of the series lines are in the ultra-violet, there will be cumulative continuous absorption on the short wave-length side. Hence, as a rule long waves will come from deeper layers, short waves from higher layers. How satisfactorily this view accounts for the distribution of energy in the solar spectrum will be evident from the following passage: "Both the observed curves of distribution of energy in the solar spectrum (by Wilsing and Abbot)

Element.	Last Series-line in the Fraunhofer Spectrum.	Corresponding Wave Number of final Orbit.
H	H ϵ , $\nu = N \left\{ \frac{1}{2^2} - \frac{1}{7^2} \right\}$	2238
	H ζ , $\nu = N \left\{ \frac{1}{2^2} - \frac{1}{8^2} \right\}$	1714
Na	$2p_1 - 6d$, $\lambda = 4668.60$	3062j
	$2p_1 - 6s$, $\lambda = 4751.89$	3437f
Mg	$2P - 6D$, $\lambda = 4351.94$	3649
Ca	$2P - 4D$, $\lambda = 5188.85$	6385j
	$2P - 5S$, $\lambda = 4847.29$	5028f

agree in having a much more pronounced peak than the black body curve, in being depressed below the latter in the violet (*the drop of intensity on the violet side of the maximum being very sudden*), and in coinciding with the black body in the extreme infra-red" (Milne, Phil. Trans., A, vol. 223, p. 218).

Thus for different rays we have different photospheres, but the distances separating the extreme photospheres probably do not differ by so much as 100 km. The photospheres and the reversing layers thus get very much mixed up. Owing to the rapid density gradient of luminous matter (except probably in the case of such atoms as are maintained by selective radiation pressure) the luminosity of the concentric layers round the sun decreases very rapidly. For example, it is well known that if, when obtaining the Fraunhofer spectrum, exposures of longer duration than 1/100 sec. are given, there is no contrast, all dark lines becoming bright. But to obtain the spectrum of layers about 100 km. from the disc during total solar eclipses, exposures of 4 to 10 sec. are required. This shows that the so-called dark lines of the Fraunhofer spectrum are intrinsically 100-1000 times more luminous than the bright lines of the flash. Hence when we expose for the Fraunhofer spectrum, the time of exposure is too short for the chromosphere, which does not, therefore, contribute anything to the resulting photograph. In other words, Fraunhofer absorption is caused by layers close to the disc, the higher chromosphere contributing nothing to the process.

These ideas may be extended to stars. According to a rough calculation, if n is the quantum number corresponding to the last absorption line of the Balmer series in a star, $n \propto \left(\frac{T}{P} \right)^{\frac{1}{2}}$. I have been able to collect the data for three A-type stars, α Cygni (ab. mag. -4.5), α Lyrae (ab. mag. $+0.6$), α Canis Majoris (ab. mag. $+0.9$). In α Cygni, 24 Balmer lines are developed, in Vega 17 (up to H ρ), and in Sirius 13. Now α Cygni is a typical giant star, Sirius is a typical dwarf, and Vega lies between them. It is generally admitted that the pressure in the reversing layer of giants is much lower than in dwarfs, and hence the great development

¹ See Russell, *Astrophysical Journal*, vol. 55, p. 130. According to some authors, H ϵ is the last absorption-line of the Balmer series. It is always difficult to trace the last line, as it is usually very faint.

of Balmer lines in α Cygnus can be easily understood. Sirius also shows more Balmer lines than the sun and this is to be ascribed to the joint action of higher temperature and lower pressure in its atmosphere.

For an exact estimation of the pressure from such data

we must wait for further theoretical and experimental work. Much of the idea contained in this communication is to be found in papers by Fowler (*Phil. Mag.*, vol. 45, p. 20), Urey (*Astro. Journ.*, Jan. 1924), Wright (*NATURE*, vol. 109), Becker (*Z. f. Physik*, vol. 18, p. 335).

27. IONISATION IN STELLAR ATMOSPHERES AND STERIC FACTOR

(a reply to Mr. M. C. Johnson)

(*Mem. Nat. Roy. Astro. Soc.*, 85, 977, 1925)

In a paper entitled "Cumulative Ionisation in Stellar Atmospheres,"¹ Mr. Martin C. Johnson has criticised certain views of the present writer regarding the so-called "steric factor." On going through the matter in detail, I find that his criticisms cannot be upheld. I shall take his criticisms one by one.

Objection 1 (in Mr. Johnson's words):

"The principal difficulty in Saha's theory of the steric factor is that it applies to all forms of ionisation equally due to radiation, thermal energy, and applied field energy; it should, therefore, lead to all experimental values of ionisation potentials being lower than the values deduced from convergence frequencies of spectra in the case of most elements. The tabulations of data (e.g. Foote and Mohler) show no such discrepancies that could be interpreted as more than naturally distributed errors."

In the electrical experiments on ionisation potential the vapour is bombarded by electrons subjected to a gradually increasing voltage, and the current voltage curve plotted (after due precautions). The particular voltage at which a sudden increase occurs in the current is taken as the ionisation potential. Whatever the steric factor may be, the vapour cannot be ionised, and no sudden kick will occur in the curve as long as the E.M.F. impressed on the electrons do not reach the required value, i.e. the ionisation potential. For an element having a large steric factor the current at this point may be larger, but the position of the kick will remain unchanged.

Hence there is no reason why the electrical experiments should give a lower value of the ionisation potential for elements with large steric factors.

Objection 2:

"Saha gives the steric factor large for C and small for Mg. The I.P. of Mg is 7.65; for C it is quoted by Professor

Fowler as from 7 to 8 volts, on a suggestion due to Saunders. On the theory of the steric factor, C^+ should appear at a lower temperature than Mg^+ in a stellar sequence; but whereas Mg^+ appears in G0 stars, C^+ does not appear till B0 or B8."

Even assuming that C has the same I.P. as Mg, which appears to me rather doubtful, it appears that Mr. Johnson has overlooked another point of great importance. Mg^+ is detected in stellar spectra by the line $\lambda=4481$, which corresponds to the combination ($3d-4f$). Now, in order that an Mg^+ atom may absorb this line, it must be brought from the 1S stage to $3d$ stage, which means an additional potential of 9 volts (15.02, I.P. of Mg^+ - 6.1, the voltage corresponding to $3d$ term of Mg^+ , which according to Fowler, is 49776). But in the corresponding case C^+ , the element is detected by the line $\lambda=4267$, which, according to Fowler, belongs to $3d-mf$ combination. In order that C^+ may be enabled to absorb this line, it must be brought from the normal state of C^+ to the $3d$ stage. According to the figures given by Fowler this corresponds to a potential of $24.28-6.29=17.99$ volts. This is just double the corresponding excitation voltage of Mg^+ . Thus this objection of Mr. Johnson seems to be quite invalid.

Objection 3:

"Again, N, an element with a high steric factor, according to Saha, persists as absorption lines of the neutral atom as far as stars of the class Oe5, with the maximum at B2. C^+ having a maximum at the same place in the stellar sequence and beginning and persisting similarly. Now the I.P. of N is variously estimated at from 17 to 30 volts in any case less than the second I.P. of C^+ , which is given by Professor Fowler as $24.3+7$ or 8 volts. But on Saha's theory the steric factor reducing the effective ionisation for N is greater than for C, i.e. N should be more easily ionised even if the ionisation potentials were the same."

Probably Mr. Johnson has the line $\lambda=3995$ in mind

¹ M. N., 84, 516, 1924.

which, up to this time, was attributed to neutral nitrogen. In my paper (*Phil. Mag.*, **44**, 1138, 1922) I pointed out that since these groups of lines do not occur in classes other than A_0 , they are most probably due to N^+ .

This prediction has been verified by Fowler's² recent work on the spectrum of ionised nitrogen, and he has now definitely assigned $\lambda=3995$ and other associated lines to N^+ . The I.P. of neutral nitrogen is still unknown, but recent work by Kiess³ indicates that it is in the neighbourhood

of 12 volts. The I.P. of N^+ is also unknown, but Fowler estimates it to be about 24 volts, so that the excitation potential for the line $\lambda=3995$ is $12+24-8.5=27.5$ volts, while the corresponding quantity for the C^+ line $\lambda=4267$ is $7+24-6.1=24.9$ volts. Thus the nitrogen lines present not only no difficulty to the theory of steric factor, but they probably justify the theory. We must, however, wait till the I.P. of C, N, and N^+ are accurately determined.

Physics Department,
Allahabad University:
1925 August 14.

² Fowler, *Proc. Roy. Soc. Lond.*, **107**, 1925.

³ Kiess, *Zeits. für Opt. und Spekt.*, **22**, 1925.

28. INFLUENCE OF RADIATION ON IONISATION EQUILIBRIUM

MEGHNAD SAHA AND RAMANI KANTA SUR

(*Nature*, **115**, 377, 1925)

In considering ionisation equilibrium of the type $M \rightleftharpoons M^+ + e - U$, the usual method adopted is to write down the entropies of M, M^+ , and e from the quantum theory, and then the law of reaction isochore is obtained from the equation $S+S'-s=U/T$. In this way we obtain the law of ionisation equilibrium

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad (1)$$

The system is regarded as binary (one-component), i.e. all the reacting electrons as well as M are derived from the ionisation of M, but when there is excess of electrons, the system is binary and the equilibrium is expressed by the form first given by H. N. Russell, namely,

$$\log \frac{x}{1-x} \cdot \frac{x'}{1+x'} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad (2)$$

The process is regarded as an abrupt one, M-atoms passing directly under the influence of heat to the M^+ -stage, without going through the intervening metastable states. Darwin and Fowler have attempted to include these intervening states by adding to the right-hand side of equation (1) a function B/T . Prof. Russell has pointed out that neither equation (1) nor (2) can be regarded as final, because it fails to take account of the possible influence of radiation and excitation of higher states. We may introduce the matter in the following way. Suppose we have a mass of sodium-vapour in the solar chromosphere. Then the ionisation of sodium atoms is determined not only by the temperature of the chromosphere (say 5000°C.), but also by the intensity of photospheric radiation of wave-length λ less than the wavelength

of the limit of the P series, passing through these sodium atoms. This radiation has a higher temperature than the local temperature; hence, as was first pointed out by Minot, we have no thermodynamic equilibrium in the solar chromosphere. The excited states are produced under the joint influence of temperature of the chromosphere and of the photospheric radiation passing through the chromosphere. To the same class belongs the absorption experiments of Wood and others, in which a column of sodium or other vapour is acted on by light of much greater intensity than what would be produced at the temperature of the absorbing gas. Here all the excited atoms, or ionised atoms, are produced by light only, and almost none are due to temperature.

The general problem has been thus attacked. In all photochemical reactions the equilibrium is determined by the intensity of light, and in treating these cases from the point of view of the phase rule, Smith expressed the opinion, without however giving his reason, that the ordinary Gibbs formula, $F=C+2-P$, must be replaced by $F=C+3-P$. We, however, arrive at the same result by assuming that the number of components has increased by one, the photochemically active light being regarded as a new and independent component. In other words, when a neutral sodium-atom passes to the $2p$ -stage by absorbing the $h\nu$ -pulse of D-radiation, then either the excited state of sodium or the pulse of light may be regarded as a new component, except when the light is defined from the effect of temperature prevailing in the gas. In the latter case, the system is a system of one component, as in the corresponding case of free electrons in equation (1).

We thus regard excited sodium-atoms as a compound, in a special sense, of normal sodium-atoms and D-pulse. It has been possible to deduce the equilibrium conditions in such cases by combining the methods given by S. N. Bose (*Zs. f. Physik*, vol. 27, p. 384) and P. Ehrenfest. We give only the final results. If ρ_ν be the density of radiation which is absorbed, and if n_1 and n_2 be the concentration of atoms in the normal and excited states,

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{\rho_\nu}{8\pi(h\nu^3/c^3) + \rho_\nu} \dots\dots\dots (3)$$

When the light is derived from the temperature of the system we can put

$$\rho_\nu = 8\pi \frac{h\nu^2}{c^3} \frac{1}{e^{h\nu/kT} - 1},$$

and we have

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-h\nu/kT}, \dots\dots\dots (3a)$$

as is usually obtained from direct application of Maxwell's law, and g_1, g_2 are the weights of the two states. If ρ_ν is very large

$$\frac{n_2}{n_1} = \frac{g_2}{g_1}, \dots\dots\dots (3b)$$

as we can expect from the definition of g_1 and g_2 .

In the case of ionisation, let ν be the frequency of ionising radiation (supposed monochromatic). Then the law of ionisation is given by

$$\log \frac{x^2}{1-x^2} P = -\frac{(U-Nh\nu)}{2.3RT} + \log \left(\frac{\rho_\nu}{8\pi(h\nu^3/c^3) + \rho_\nu} \right) + \frac{5}{2} \log T - 6.5, \quad (4)$$

where $N=R/k$.

If

$$\rho_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1},$$

i.e. radiation is due to the temperature of the system, (4) reduces to

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5, \quad (4a)$$

as is obtained directly from thermodynamical theories.

Equation (4) expresses equilibrium in a two-component system, equation (4a) in a one-component system.

Of course the ionising power is not limited to one single radiation, nor are all pulses of frequency $\nu > \nu_0$ (ν_0 =convergence frequency of the principal series) equally effective in causing ionisation. But these facts can be taken into consideration in the method used above.

Allahabad, India,

January 21.

29. THE PHASE RULE AND ITS APPLICATION TO PROBLEMS OF LUMINESCENCE AND IONISATION OF GASES

(*Journ. Ind. Chem. Soc.*, 2, 49, 1925.)

The phase rule was discovered by the great American physicist, Willard Gibbs, in the year 1877, but was first popularised by W. Ostwald in the year 1894, in his *Wissenschaftliche Klassiker*. Since this date, it has formed one of the corner-stones of the science of physical chemistry, and has served as an invaluable guide for the study of problems of gaseous equilibrium, and changes of state.

The present author has shown¹ about four years ago that a thermal stimulus alone can excite atoms to luminescence and ionisation, and how these problems can be treated thermodynamically. A serious defect of these theories is that radiation which plays an essential part in determining the equilibrium cannot be taken into account. The theory has been extended by Russell in America²,

Darwin, Fowler and Milne^{3,4}, in England and by Enskog⁵ and Becker⁶ in Germany. But though many essential improvements have been made, none of the attempts to include radiation as a factor in determining the equilibrium can be said to have met with success.

The object of the present paper is to present the ionisation theory from the standpoint of the phase rule. The phase rule states that if in a gaseous system C=number of independent components, P=number of phases, F=number of degrees of freedom, then

$$F = C + 2 - P \dots\dots (1)$$

¹ M. N. Saha, On a Physical Theory of Stellar Spectra, Proc. Roy. Soc., Lond. (1921), Vol 99, p. 135.

² H. N. Russell, The Astrophysical Journal, Vol. 55, pp. 119-144.

³ C. G. Darwin and R. H. Fowler, The Philosophical Magazine, Vol. 45, Page 1, 1924.

⁴ R. H. Fowler and E. A. Milne, Proc. Phys. Soc., London, Vol. 35, p. 94.

⁵ Enskog, Annalen der Physik, Band 72.

⁶ R. Becker, Zeitschrift für Physik, Bd. 18, 325, Vol. 28, p. 258.

Case 1. Take Ca-metal which is heated in a closed vessel. We neglect the intermediate stages, and consider simply the equilibrium



the neutral atoms directly dissociating into the positively charged atom and the electron. We suppose that the vessel emits no electrons.

Here we have $C=1$, because the concentration of electrons is determined by the fraction x of original Ca-atoms ionised. $P=1$ (all are in the gaseous phase). Variables — T , p , and x (fraction ionised). From the phase rule,

$$F=1+2-1=2,$$

i.e., when 2 variables are given, say T and p , the third, x , is automatically determined. The equation connecting x , T and P is the well known law of ionisation.

$$\log \frac{x^2}{1-x^2} P' = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots (3)$$

Case 2. Ionisation of calcium gas in an atmosphere containing an excess of electrons.

This is a two component system, the independent components being Ca^+ (concentration y), e (concentration x), Ca-atoms may be regarded as a compound of Ca^+ and e . The variables are now T , p , x and y .

Consequently, $F=C+2-p=3$.

Now we have four variables, and the number of degrees of freedom 3. Hence there must be one equation connecting the variables T , p , x and y . This is the equation first given by Russell.⁷

$$\log \frac{P_{\text{Ca}^+} P_e}{P_{\text{Ca}}} = K \quad \dots (4)$$

P_{Ca^+} = partial pressure due to Ca^+ atoms,

P_e = partial pressure of electrons, etc.,

Now,

$$P_{\text{Ca}^+} = yRT, P_e = xRT, P_{\text{Ca}} = (1-y)RT$$

$$P = P_{\text{Ca}^+} + P_e + P_{\text{Ca}} = (1+x)RT.$$

Hence

$$P_{\text{Ca}^+} = \frac{y}{1+x} P, P_e = \frac{x}{1+x} P, P_{\text{Ca}} = \frac{1-y}{1+x} P.$$

Thus

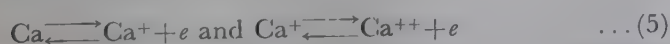
$$\log \frac{x}{1+x}, \frac{y}{1-y} p = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots (4')$$

where U = heat of ionisation.

Case 3. Double Ionisation.

Let us now treat the case when calcium vapour is heated within an enclosure to such a temperature, that not only is calcium ionised to Ca^+ and e but some fraction of Ca^+ is also ionised to Ca^{++} and e .

The reactions are now

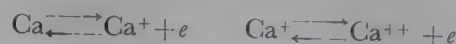


taking place simultaneously from Ca-vapour alone. This is a one component system, because the products, if all reduced to absolute zero, would yield only Ca-atoms leaving no excess of electrons.

The variables are T , p , x and y , where x , fraction of atoms ionised to Ca^+ and y , fraction ionised to Ca^{++} . There is only one phase. From the phase rule,

$$F=1+2-1=2.$$

There are four variables, but the number of degrees of freedom is two. Hence we must have two independent equations. These are the equations of mass action representing the two reactions



We have

$$\log \frac{P_{\text{Ca}^+} P_e}{P_{\text{Ca}}} = K, \log \frac{P_{\text{Ca}^{++}} P_e}{P_{\text{Ca}^+}} = K' \quad \dots (6)$$

Now

$$P_{\text{Ca}} = (1-x-y)RT, P_{\text{Ca}^+} = xRT, P_{\text{Ca}^{++}} = yRT$$

$$P_e = (x+2y)RT \text{ and hence } P = (1+x-2y)RT.$$

Hence

$$\log \frac{x(x+2y)}{(1+x+2y)(1-x-y)} P = -\frac{U_1}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots (6')$$

$$\log \frac{y(x+2y)}{x(1+x+2y)} P = -\frac{U_2}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots (6'')$$

since p and T are given, x and y are perfectly determinate.

Case 4. Double ionisation, but concentration of electrons is now arbitrary.

The variables are now T , p , x , y and f , where

x = fraction of Ca atoms ionised to Ca^+

y = " " " " Ca^{++}

$$f = \frac{\text{concentration of electrons}}{\text{concentration of original Ca atoms.}}$$

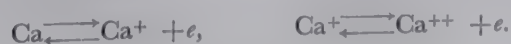
The number of independent components is now two, for if the system be reduced to absolute zero, we shall be left with Ca atoms and an excess of electrons.

Phase = 1 (gaseous).

Hence from the phase rule

$$F=C+2-P=3.$$

We have five variables, but the number of degrees of freedom is 3. Hence we must have two independent equations. These are the equations of mass action representing the reactions



⁷ H. N. Russell, *loc. cit.*, p. 144.

The equations now take the forms:

$$\log \frac{x}{1-x-y}, \frac{f}{1+f} = K = -\frac{U_1}{2.3RT} + \frac{5}{2} \log T - 6.5$$

$$\log \frac{y}{x} + \frac{f}{1+f} = K' = -\frac{U_2}{2.3RT} + \frac{5}{2} \log T - 6.5 \quad \dots (7)$$

U_1 and U_2 = heats of first stage and second stage ionisation respectively.

From these two equations, it will appear that x and y cannot be determined unless f is known. This fact may have an interesting application in the problem of successive disappearance of lines of Si, Si⁺, Si⁺⁺ and Si⁺⁺⁺ in stars, because in high temperature stars, f must be abnormally high, and we may put

$$\frac{f}{1+f} = 1$$

For treble ionisation in an atmosphere of excess of electrons, the equations will take the form

$$\log \frac{x}{1-x-y-z} \cdot \frac{f}{1+f} = K_1$$

$$\log \frac{y}{x} \cdot \frac{f}{1+f} = K_2 \quad \dots (8)$$

$$\log \frac{z}{y} \cdot \frac{f}{1+f} = K_3$$

If we change the notation a little, we can express the formula in a symmetrical form. Let $x_0, x_1, x_2, x_3 \dots x_n$ denote the fraction of Ca atoms which are respectively neutral, singly ionised, doubly ionised, etc.

then $x_0 + x_1 + x_2 + x_3 + \dots + x_n = 1$
and let f denote the ratio concentration of electrons to the original number of Ca atoms.

then we have

$$\left. \begin{aligned} \log \frac{x_1}{x_0} \cdot \frac{f}{1+f} &= K_1 \\ \log \frac{x_2}{x_1} \cdot \frac{f}{1+f} &= K_2 \\ \log \frac{x_3}{x_2} \cdot \frac{f}{1+f} &= K_3 \end{aligned} \right\} \dots (8')$$

It is clear that the method might be extended to cover such cases as the reaction of any positively charged particle with any negatively charged particle which need not necessarily be an electron. We have been assuming so far that an ionised metal ion, say Ca⁺, can only combine with an electron, but there is no reason why Ca⁺ will not combine with a negatively charged atom like Cl or O, giving us a Ca⁺ Cl⁻ or Ca⁺ O⁻ molecule having its

characteristic band spectrum. The Cl ion will be as likely to combine with a positively charged particle as a free electron. But as we know nothing about the spectroscopy of such processes, no purpose will be served by putting down the equations. The suggestion is thrown here simply to account for the non-recurrence of the lines of electro-negative gases like Cl, Br and I in the solar spectrum, and for the occurrence of a large number of lines showing a band structure, *e.g.*, the bands ascribed to CN.

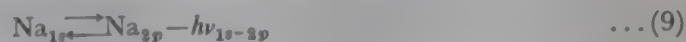
Radiation as a factor in determining the equilibrium

As has been pointed out on several previous occasions, radiation must play a very essential role in determining the equilibrium. For there are an infinite number of metastable quantum orbits between the normal state and the ionised state. In passing from the normal to the ionised state, the atom may pass through these states. As radiation pours through the normal atom, the pulses belonging to the principal series are absorbed, and the atom passes to the metastable state. It is easier to ionise the metastable states, *e.g.*, in the case of a sodium atom in the 2*p* stage, the ionisation potential is 2.6 volts. The percentage of ionised Na atoms will therefore be materially affected by the density of radiant energy in the space corresponding to the characteristic lines of Na.

It is evident from the above that in addition to considering reactions of the type



we have also to consider such reactions as



i.e., radiation ν_{1s-2p} enters into the equilibrium. These are quite new types, and I have yet no clear idea how to tackle these problems. Yet a few casual remarks may be made.

Smit⁹ expresses the opinion that in the analogous case of photo-chemical equilibrium, besides T and p , the intensity of light will also appear as a new variable. The phase rule must then be modified from the form

$$F = C + 2 - P \text{ to the form } F = C + 3 - P$$

But no theoretical argument is given. We may regard Na_{2p} as a new component, if excess of ν_{1s-2p} pulses be present. There is no objection in calling Na_{2p} or any other excited state of Na as a new component, because the ionisation potential, consequently the chemical properties of the excited atom are widely different from those of the normal atom. We have then from $F = C + 2 - P$, since $C = 2$ and $P = 1$, $F = 3$ or the number of degrees of freedom is three, T , p , and the intensity of light. The cases can now be subdivided into two broad categories:—(1) Cases

⁸ Pringsheim, Physik der Sonne, p. 116.

⁹ Smit, The Theory of Allotropy, Chap. VII, p. 177.

in which we start with Na atoms only, and the proportion Na_{2p} , or the $h\nu_{1s-2p}$ pulses is determined by the value T and p only. We may say that in such cases, the radiation is in equilibrium with matter at this temperature. (2) Cases in which Na atoms, otherwise all in the $(1s)$ orbit, are illuminated by $(1s-2p)$ pulses. The proportion of Na_{2p} atoms will now be completely determined by the intensity of $(1s-2p)$ pulses. To this class belong the various absorption experiments performed by Wood, Bevan and others. (3) Classes intermediate between the two, *e.g.*, the solar chromosphere, where T is sufficiently high to convert Na_{1s} atoms to Na_{2p} states, but in addition, there are the $1s-2p$ pulses pouring from the photosphere. Here the equilibrium will depend upon T , p and the intensity of light. That the chromosphere is not in a state of thermodynamic equilibrium was first pointed out by E. A. Milne in a recent letter to *Nature*.

It is evident that instead of Na_{2p} atoms, the reacting pulse of light $\nu=1s-2p$ may be looked upon as a new component.

The range within which a particular state may occur.

In this connection it is necessary to add a few words regarding the thermodynamical range within which a particular metastable state may occur. To introduce the matter we may begin with a general examination of the effect of heat on matter. The states succeeding each other may be visualized in the following scheme given by me a few years ago.

HYDROGEN

State	Phenomena
Solid	
↓	Fusion
Liquid	
↓	Vaporisation
Gas (molecular)	
↓	Dissociation
Atomic state	
↓	Luminescence
Excited states of atoms	
↓	Ionisation
Positively charged atom	

example, camphor vaporises directly without melting at all. Water can be obtained in the liquid form between 0°C and 100°C under the conditions prevailing in this globe of ours, but if the experimenter is transported to the moon, where the pressure is, say only 2 mms. of mercury ice would behave just like camphor and vaporise without melting at all. The experimenter on the moon would have to increase the pressure artificially to get the liquid stage. A similar case is that of carbon which vaporises without previously melting but Lummer and others¹⁰ claim that they have obtained the liquid stage by heating carbon under great pressure.

The analogy may be extended further. In the cases of tungsten, platinum and other metals, the metal emits electrons even in the solid state.

The problem we are discussing here is the range of experimental conditions in temperature and pressure, within which a metastable state, say $2p$ or $3d$ of sodium or any other element may occur. It has been recorded by several observers that it is very difficult to obtain the exact experimental conditions at which the $2p$ or $3d$ orbits would occur in sufficient proportion to give us the diffuse and the sharp lines in absorption. At low temperatures the stimulus is not sufficient to produce an appreciable number of Na_{2p} atoms. If the temperature be sufficiently raised, they pass directly into ionised condition. The intermediate states may be obtained by combining high temperature with high pressure, or using a very long column of vapour at comparatively low temperature and low pressure. A similar phenomenon is well known to spectroscopists in the case of the spectra of C and Si. The ionised spectra of these elements have been studied in great detail, but it is very difficult to get lines of the neutral atoms. Only a few lines are recorded¹¹. Probably when carbon and silicon vaporise directly from the solid state, a large percentage of them are ionised or there is not much range for the metastable states of C or Si to be developed. Even when the spectra are obtained from vacuum discharge through their volatile compounds, they split more readily into C^+ , or C^{++} than into the neutral form. Attempts are being made to study these phenomena experimentally.

The author had many opportunities of discussing the subject-matter (from the standpoint of the physical chemist) with his friend Dr. N. R. Dhar, and wishes to record here his sincere thanks.

DEPARTMENT OF PHYSICS,
ALLAHABAD UNIVERSITY
Received April 22, 1925.

¹⁰ Kohn—Zeitschrift für Physik, Vol. 27 (1924), p. 305.

¹¹ T. R. Merton and R. C. Johnson, Proc. Roy. Soc., London, Vol. 103, p. 394.

It does not always follow that the succeeding stages occur in the order given above. Thus, to take a familiar

30. THE SPECTRUM OF Si^+ (ONCE IONISED SILICON)

(*Nature*, **116**, 644, 1925)

PROF. A. FOWLER has recently shown that the spectrum of Si^+ is similar in constitution to that of Al, that is, consists of doublets having $2p_2, 2p_1$, as the highest terms. A number of lines, ascribed by Fowler to Si^+ , remain, however, well outside his scheme of classification, and some of these can be arranged in a group of quartets.

MULTIPLY I

j	1	2	3
1	(0) 17154.38 .. 116.0 .. 17038.38 62.19	(1) 62.25	
2	(2) 17216.57 .. 115.94 .. 17100.63 .. 199.89 .. 16900.74 134.56 134.96	(0) 17235.19 .. 199.49 .. 17035.70	(1)
Interval ratio	116.00 : 199.89 = $\frac{2.9}{3} : \frac{5}{5}$ observed (Landé) 62.20 : 134.76 = $\frac{2.3}{3} : \frac{5}{5}$ observed (Landé)		

This is a pp' -combination.

The intensity rule is only roughly obeyed.

MULTIPLY 2

j	1	2	3
1	(1) 18382.63 .. 116.48 .. 18266.15 339.49	(0) 339.11	
2	(0) 18043.14 .. 116.10 .. 17927.04 .. 199.86 .. 17727.18	(1)	(2)

This seems to be an intercombination between doublet P and quartet p -terms. But none of the known doublet P 's has 339 as frequency difference.

The differences occurring in these multiplets occur in other pairs which have not yet been classified, *e.g.*

$$\begin{aligned} (0) & 18402.19 - 18286.73 = 115.46 \\ (0) & 18415.41 - 18280.08 = 135.33 \\ (1) & 20573.45 - 20373.87 = 199.58 \end{aligned}$$

The group having the successive differences 199 and 116 correspond to p -terms of a quartet series. Evidently a quartet series is possible for Si^+ , but it is only feebly developed under the usual methods of excitation. Without more data on the spectrum of Si^+ , it is not possible to find out more information on the point.

Allahabad University.

31. ON THE ABSOLUTE VALUE OF ENTROPY*

Meghnad Saha & Ramanikanta Sur

(*Phil. Mag., Sr. VII*, **1**, 279, 1926)

According to Boltzmann, the entropy of a thermodynamical system is represented by the equation

$$S = k \log_e W \quad \dots \quad (1)$$

S =entropy, k =Boltzmann's gas-constant, W =probability of the state.

There are different ways of calculating the probability W for different thermodynamical systems. In previous years, W was used in a relative sense, in terms of some standard state. By W was meant the mathematical probability, hence it was always a fraction. Moreover, it remained indeterminate to the extent of an additive constant.

To Planck we owe the conception of the "Thermo-

*Communicated by the Authors.

dynamical probability". This is proportional to the mathematical probability, but not quite equal to it. The mathematical probability is a fraction, while the thermodynamical probability is a whole number. Planck has developed methods for calculating the thermodynamical probability of different systems—e.g., a perfect gas and black body radiation. As is well known, this idea led, in the hands of its author, to the development of the Quantum theory, which is now responsible for progress along all lines in physical science.

There are, however, a few points which are not yet clear. Some of these refer to the fundamental assumptions of the theory, others refer to the mode of application of the fundamental ideas. The exact nature of these obscure points can only be made clear by reference to the actual working, which we now proceed to do.

§ 1. Theory of Perfect Gases¹

Let us take a large number N of molecules enclosed within a volume V in the gas-kinetic sense. To calculate the probability of the system, the volume is divided into a number of cells denoted by 1, 2, 3, ... n , containing $N_1, N_2, N_3 \dots N_n$ molecules respectively. The thermodynamical probability is defined as the total number of complexions (i.e., the total number of ways in which this distribution can be effected). It is easy to see that

$$W_n = \frac{N!}{N_1! N_2! \dots N_n!} \quad \dots (2)$$

The mathematical probability

$$W_{mn} = \frac{W_n}{\sum W_n} = W_n \cdot n^{-n}. \quad \dots (2.1)$$

The summation $\sum W_n$ is taken over all positive values of N_1, N_2 , etc. consistent with the condition

$$N_1 + N_2 + \dots N_n = N.$$

$$\text{Let } \frac{N_1}{N} = w_1, \quad \frac{N_2}{N} = w_2 \dots$$

Then with the help of Stirling's formula, it can be easily shown that

$$\log W_n = -N \sum_{r=1}^n w_r \log w_r \quad \dots (3)$$

The actual or equilibrium value of $\log W_n$ is obtained by making it maximum subject to the prescribed conditions. Let ϵ_r = average energy per molecule in the cell r . Then the total energy

$$E = N_1 \epsilon_1 + N_2 \epsilon_2 + \dots N_n \epsilon_n \\ = N \sum w_r \epsilon_r = \text{const.} \quad \dots (4)$$

$$\text{and } \sum w_r = 1. \quad \dots (5)$$

From equations (3), (4), (5), we can deduce that in case of equilibrium

$$w_r = a \rho^{-\beta \epsilon_r} \quad \dots (6)$$

From the relation $\frac{\partial S}{\partial E} = \frac{1}{T}$ it can be shown that

$$\beta = \frac{1}{kT} \quad \dots (7)$$

From equations (5) and (6)

$$a = \frac{1}{\sum e^{-\frac{\epsilon_r}{kT}}}, \quad \dots (8)$$

and it can easily be shown that the free energy

$$F = kNT \log a; \quad (9)$$

a , however, remains indeterminate, and it cannot be calculated without the introduction of some further hypothesis.

By an application of Liouville's law, Planck shows that for a system obeying the canonical laws of Hamilton the motion is completely defined if the positional (q) and the momenta (p) coordinates corresponding to each individual degree of freedom of each particle are given. In this case he shows that the phase integral

$$H = \dots \iiint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f \quad (10)$$

(the integral being taken for all the degrees of freedom for a particle), remains unchanged by subsequent events. H is known as the extension of the elementary region of the phase space. According to classical theory, H may have any infinitely small value up to zero, but according to the quantum theory H has always got a finite, though small, invariant value.

The summation $\sum e^{-\frac{\epsilon_r}{kT}}$ can now be effected.

$$\sum e^{-\frac{\epsilon_r}{kT}} = \frac{\sum e^{-\frac{\epsilon_r}{kT}} dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f}{H}, \quad \dots (11)$$

For monatomic gases, H must refer to the representative particle in the cell r , having the coordinates x_r, y_r, z_r , and velocity components u_r, v_r, w_r .

$$\text{Taking } \epsilon_r = \frac{1}{2} m(u_r^2 + v_r^2 + w_r^2) + \epsilon_0, \quad \dots (12)$$

where ϵ_0 denotes the unalterable internal energy of an atom at rest, and

$$dp_1 dp_2 dp_3 = m^3 du_r dv_r dw_r.$$

We obtain

$$\sum e^{-\frac{\epsilon_r}{kT}} = \frac{V}{H} e^{-\frac{\epsilon_0}{kT}} (2\pi mkT)^{\frac{3}{2}} \quad \dots (13)$$

With this value of $\sum e^{-\frac{\epsilon_r}{kT}}$, neglecting ϵ_0 ,

$$S = kN \left\{ \frac{V}{H} (2\pi mkT)^{\frac{3}{2}} \right\} + \frac{3}{2} kN \quad \dots (14)$$

¹ The subject matter of this section is merely an abstract of §113-§134 of Planck's 'Warmestrahlung,' 5th edition.

According to the classical gas laws,

$$S = kN \log \{VT^{\frac{3}{2}}\} + i, \quad \dots (14.1)$$

where i is independent of T and V , but depends upon N . As far as the calculation of gas laws and specific heat is concerned, the exact value of i is immaterial; but if we wish to study the chemical behaviour of the gas, the vapour pressure, etc., the knowledge of i is essential, as was first pointed out by Nernst in connexion with his Heat Theorem.

Now to show how i depends upon N we take p identical vessels, each of volume V , containing the same quantity of the same gas side by side. Then suppose the sides be made to collapse suddenly and the p volumes are made to mix with each other. No change has been made in the system. The entropy can be calculated by adding the entropies of the p vessels, each of volume V . Thus for the entropy of the whole gas occupying the volume pV we have

$$S = kNp \log (VT^{\frac{3}{2}}) + pi(N), \quad \dots (14.2)$$

and this must equal

$$k\overline{N}p \log (\overline{pV} \cdot T^{\frac{3}{2}}) + i(pN),$$

which is the entropy of a gaseous mass of $\overline{pN}$ particles occupying the volume $\overline{pV}$.

$$\text{Hence } pi(N) = kNp \log p + i(pN).$$

The above relation is satisfied if

$$i(N) = -kN \log N.$$

Thus we can deduce from the classical theory that

$$S = kN \log \left[\frac{V}{N} T^{\frac{3}{2}} A \right] \quad \dots (14.3)$$

where A is independent of N , T , and V .

From Planck's theory, we have

$$S = kN \log \left[\frac{V}{h^3} (2\pi mkT)^{\frac{3}{2}} \right] \quad \dots (14.4)$$

Comparing the two expressions, we find that H must vary as N . Planck puts $H = Nh^3$. But this is, however, not quite clear from the expression for H , for

$$H = \frac{\int \int dq_1 dp_1 dq_2 dp_2 dq_3 dp_3}{= h^3}, \quad \dots (15)$$

if we put, according to the canons of the quantum theory,

$$\int \int dq \cdot dp = h \text{ (Planck's constant).}$$

Sackur and Tetrode², who were the first to calculate the value of i , proceeded in a different way. According to Sackur the thermodynamic probability is not equal to our W_n , but it is equal to

$$\frac{W_n}{N!} \text{ or } \frac{1}{N_1! N_2! \dots N_n!}$$

The value of H , according to Sackur, is

$$\int \int dq_1 dp_1 dq_2 dp_2 dq_3 dp_3 = h^3.$$

Tetrode's procedure was identical.

Attention to this point has recently been called by Ehrenfest and Trkal³, who have introduced a new method of dealing with the thermodynamical problems, *e.g.* dissociation equilibrium and vapour pressure, in which all these difficulties are avoided. We shall return to this method shortly. Planck has justified his assumption, *viz.*, $H = Nh^3$, by taking into account the permutability of the molecules, but the reasoning is rather difficult to follow.

§2. Ehrenfest's Method.

Ehrenfest has introduced a very general method for dealing with the thermodynamical behaviour of different and complex systems, like mixtures of gases reacting with each other. We shall confine our attention to the case of perfect gases.

Ehrenfest replaces the entropy function S by another function $\{\gamma\}$ which is allied but not equal to W . $\{\gamma\}$ is supposed to represent the total phase space described by the system and is defined in the following way:—Let the system consist of N particles. Then each particle describes a sub-phase space $\{\mu\}$, where

$$\{\mu\} = \dots \int \int \dots dq_1 dp_1 dq_2 dp_2 \dots dq_r dp_r, \quad \dots (16)$$

The total $\{\gamma\}$ -space described by the system is then given by

$$\{\gamma\} = P \prod_N \{\mu\}, \quad \dots (17)$$

the product extending over all the particles. P represents the permutability of the particles.

Now, in our case, *i.e.*, for monatomic gases,

$$\{\gamma\} = \dots \int \int \int \dots dx_r dy_r dz_r d(\mu_r v_r) d(mv_r), \quad (17.1)$$

$$\mu_r = p_{1r}, \quad mv_r = p_{2r}, \quad mw_r = p_{3r}.$$

$$\text{Now } \Sigma p_{1r}^2 + p_{2r}^2 + p_{3r}^2 = 2mE, \quad \dots (17.2)$$

where E = total kinetic energy and m is the mass of a particle.

$$\text{Hence } \{\gamma\} = \frac{V^N (2\pi mE)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \quad \dots (18)$$

$$\text{Putting now } E = \frac{3N}{2} kT,$$

$$\log \{\gamma\} = N \log \{V (2\pi m kT)^{\frac{3}{2}}\} \quad \dots (19)$$

According to Sackur-Tetrode:

$$\begin{aligned} S &= kN \log \left\{ e^{\frac{5}{2}} \frac{V}{N h^3} (2\pi m kT)^{\frac{3}{2}} \right\} \\ &= k \log W. \end{aligned}$$

² Sackur, *Ann. d. Physik*, xl; Tetrode, *loc. cit.* xxxix.

³ Ehrenfest and Trkal, *Proc. Amst. Akad.* xxiii. (1920).

Comparing the two expressions,

$$W = \frac{\{\gamma\}}{h^{3N} N!} \dots (20)$$

§ 3

Ehrenfest and Trkal have not traced any connexion between $\{\gamma\}$ and W . But from equations (18), (19), and (20), it is possible not only to connect W and $\{\gamma\}$ for any general system, but also to lay down a general theorem for the calculation of the probability of any system. This we now proceed to do.

According to Planck, the probability W is a whole number. But whenever in physics we wish to determine the absolute value of any quantity, we must as well lay down a "unit" for it. Now let us see what is meant by "Unit Probability."

The idea of "Unit Probability" is intimately connected with the zero of entropy; for $S = k \log W$, and when $W = 1$, $S = 0$. According to the second law of thermodynamics, this takes place when a condensed system is reduced to absolute zero; for a reversible engine acting between this system and another system at a finite temperature T will be able to convert all the heat energy abstracted into mechanical work.

We can suppose this to take place in another way. Suppose we have a gas at a finite temperature. The particles are moving in a chaotic way and at a distance from each other. Suppose all of them suddenly begin to move with identical velocity in the same direction, with the proviso, however, that the total kinetic energy remains the same. Then if this system, on coming into contact with another body and suffering inelastic collision, transfers the whole of its energy to that body, we can say that the heat motion has been completely converted into mechanical work. Thus the idea of absolute zero, and zero of entropy, presupposes a system of particles absolutely devoid of all motion. But this is not sufficient. If the particles which are devoid of all motion remain at a distance from each other, then, owing to mutual attraction and there being no motion, they will begin to move towards each other, and kinetic energy will again be developed and can again be converted into mechanical work. For an attracting system, motion, and with it the energy available from the system, will entirely stop when the particles are packed together in the closest manner possible.

We assume that such a system possesses unit probability. Let the value of γ -space for such a system be denoted by $\{\gamma\}$.

We may remark here that these considerations apply only if we regard the atoms as the final constituents of matter. This, however, is not the case, and therefore, even when the state pictured above has been reached, the electrons of one atom will react mechanically on the other atoms and

electrons; and motion will never be entirely absent. Thus we cannot conceive of an absolute zero of temperature unless we picture to ourselves a state in which the protons and electrons have combined in some unknown way and annihilated all matter. We can therefore talk of absolute zero in a world where there is no matter. But according to the generalized theory of relativity, there can be neither space time, nor any physical quantity in a world which is entirely devoid of matter. Hence we come to a conclusion which has been previously reached by Nernst, viz., in the phenomenal world it is impossible to reach the absolute zero of temperature.

We shall now proceed to calculate the thermodynamical probability of a system in the terms of $\{\gamma\}$, as unity. The probability of the state of a system is proportional to the phase space $\{\gamma\}$ described by the system. Therefore the thermodynamical probability at a finite temperature

$$W = \frac{\{\gamma\}}{\{\gamma\}_0} \dots (21)$$

We have now to find out the value of $\{\gamma\}_0$.

Let us suppose that in the system there are N particles, each particle having f degrees of freedom. We shall follow Ehrenfest's considerations in calculating $\{\gamma\}_0$. According to the definition, for a single particle

$$\{\mu\} = \dots \iint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f = h^f \dots (16)$$

Let us suppose that each particle is a Planck-resonator and confine our attention to one degree of freedom only. According to the quantum theory its phase-point (q, p) must lie at $p=0$, $q=0$, or on one of the ellipses $h, 2h, \dots$, the area between two consecutive ellipses being given by

$$\iint dq dp = h.^4$$

Ehrenfest attaches a "weight" h to each one of these ellipses, and in particular also to the point $(p=0, q=0)$. Now, in our case, i.e., for a system at absolute zero, none of the degrees of freedom of any particle is excited: or the phase of every particle for each degree of freedom is at $(p=0, q=0)$.

Hence, for a single particle,

$$\{\mu\} = \dots \iint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f = h^f$$

For the whole system

$$\pi_N \{\mu\} = h'^N \dots (22)$$

Again the N particles can be arranged amongst themselves in $N!$ ways. Combining this with (22), we obtain

$$\{\gamma\}_0 = h'^N N! \dots (23)$$

⁴ Vide Ehrenfest and Trkal, Proc. Amst. Soc. xxiii. p. 179 (1920).

To sum up, the thermodynamic probability in Planck's sense is given by

$$W = \frac{\{\gamma\}}{h^{5N} \cdot N!} \quad \dots (20.1)$$

This will cover all cases.

On the basis of this law we shall now calculate the entropy of a system consisting of diatomic molecules.

§ 4. Entropy of a Gas consisting of Diatomic Molecules.

In this case we shall ignore the rotation of molecules about the axis of symmetry and also all internal motions of atoms in the molecule. Therefore, each molecule has only five degrees of freedom, three of these being translational and two rotational.

$$\text{Thus } \{\gamma\}_0 = h^{5N} \cdot N! \quad \dots (24)$$

where N denotes the total number of molecules considered.

Now, for a single molecule,

$$\begin{aligned} \{\mu\} &= \int \dots dx dy dz d\theta d\psi dp_1 dp_2 dp_3 dp_4 dp_5 \\ &= V \cdot 4\pi \cdot \int \dots dp_1 \dots dp_5 \end{aligned} \quad \dots (25)$$

Therefore γ -space for the total system is given by

$$\begin{aligned} \{\gamma\} &= \prod_{\mu} \{\mu\} \\ &= V^N \cdot (4\pi)^N \cdot \int \dots dp_1 dp_2 \dots dp_{5N} \dots \end{aligned} \quad \dots (26)$$

the integrals being taken for all molecules, dp_{1r} , dp_{2r} , etc. denote the momenta of the different molecules.

The total kinetic energy of the molecules being given, the integration is to be taken over all possible values of the momenta which are consistent with it. If E be the kinetic energy given, we have

$$\sum \frac{p_{1r}^2}{2m} + \frac{p_{2r}^2}{2m} + \frac{p_{3r}^2}{2m} + \frac{p_{4r}^2}{2a} + \frac{p_{5r}^2}{2b} = E, \quad \dots (27)$$

where m is the molecular mass and a and b represent the

moments of inertia. The molecules being all similar, these quantities (m , a , and b) have the same values for all the molecules. The total number of terms in the left-hand side of equation (27) is $5N$.

Hence

$$\begin{aligned} \{\gamma\} &= V^N \cdot (4\pi)^N \cdot \int \dots dp_{1r} dp_{2r} \dots dp_{5r} \dots \\ &= V^N \cdot (4\pi)^N \cdot \sqrt{\pi^{5N}} \cdot \frac{\sqrt{E^{5N-1}}}{\left(\frac{5N}{2}\right)!} \cdot (2m)^{3/2} \cdot (2a)^{1/2} \cdot (2b)^{1/2} \dots \end{aligned} \quad \dots (28)$$

since N is very large, we may put $5N$ for $5N-1$.

$$\begin{aligned} \{\gamma\} &= V^N \cdot (4\pi)^N \cdot \frac{\sqrt{2\pi E^{5N}}}{\left(\frac{5N}{2}\right)!} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N \\ &= \frac{V^N \cdot (4\pi)^N \cdot \sqrt{2\pi E^{5N}} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N}{\left(\frac{5N}{2}\right)!} \end{aligned} \quad \dots (28.1)$$

Hence

$$W = \frac{\{\gamma\}}{\{\gamma\}_0} = \frac{\{\gamma\}}{h^{5N} \cdot N!} \quad \dots (29)$$

$$= \frac{V^N \cdot (4\pi)^N \cdot \sqrt{2\pi E^{5N}} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N}{h^{5N} \cdot N! \cdot \left(\frac{5N}{2}\right)!} \quad \dots (29.1)$$

Using Stirling's formula and putting $E = \frac{5}{2} NkT$, we obtain

$$W = \left\{ \frac{e^{1/2} \cdot 4\pi V \cdot (2\pi kT)^{5/2} \cdot m^{3/2} \cdot a^{1/2} \cdot b^{1/2}}{N \cdot h^5} \right\}^N \quad \dots (29.2)$$

$$S = k \log W$$

$$= Nk \log \left\{ \frac{e^{1/2} \cdot 4\pi V \cdot m^{3/2} \cdot a^{1/2} \cdot b^{1/2} \cdot (2\pi kT)^{5/2}}{N \cdot h^5} \right\} \quad \dots (30)$$

It may be emphasized here that the theorems $E = \frac{5}{2} NkT$ for monatomic gases and $E = \frac{5}{2} NkT$ for diatomic gases have not been assumed here, but followed directly from the theory. The calculations have not been reproduced here.

32. ON ENTROPY OF RADIATION II*

MEGHNAD SAHA & RAMANI KANTA SUR

(*Phil. Mag.*, *Sr. VII*, 1, 890, 1926)

In a previous paper, it has been shown that the thermodynamical probability of a system is given by the law,

$$W = \{\gamma\} \cdot \{\gamma\}_0 \quad \dots (1)$$

Where $\{\gamma\}$ = phase-space described by the system at temperature T_0 , $\{\gamma\}_0$ = phase-space described at absolute

*Communicated by the Authors.

zero. It was shown that the absolute value of entropy of perfect gases could be deduced from this theorem.

The same formula can be applied for deducing the entropy of radiation. Since the time when Bartoli deduced the existence of radiation pressure from thermodynamical reasoning, it has been customary to look upon radiation as

a sort of perfect gas. But the analogy is often misleading, for the energy of gaseous molecules is capable of continuous variation, while according to Planck, radiant energy or energy of light pulses can vary only in multiples of $h\nu$. If $E\nu$ = total energy of frequency ν , then

$$E\nu = N\nu \cdot h\nu \quad \dots (2)$$

$N\nu$ = number of energy elements.

In calculating the probability, we have further to find out the number of ways in which a quantum can be contained within unit volume. This is equal to $A = \frac{8\pi\nu^2}{c^3}$. The deduction of this theorem forms the greatest difficulty in the theory of black body radiation. In the original method of deduction by Jeans and others, $\frac{8\pi\nu^2}{c^3}$ represents the total number of stationary waves in unit volume having their frequency between ν and $\nu+1$. It is deduced in a most complicated way from electromagnetic considerations.

Bose has recently given a very elegant and simple method of deducing the theorem

$$A = \frac{8\pi\nu^2}{c^3}, \quad \dots (3)$$

which is reproduced here.

According to modern conceptions, a pulse of light carries with it the momentum $\frac{h\nu}{c}$ in the direction of its motion. It has got the components

$$p_x, p_y, p_z, \text{ where } p_x^2 + p_y^2 + p_z^2 = \frac{h^2\nu^2}{c^2}.$$

The phase-space described by the pulse in its translatory motion is, according to Planck,

$$\dots \int \int \int dp_x dp_y dp_z \dots = \dots \int \int \int_{\nu}^{ \nu+1} dx dy dz dp_x dp_y dp_z = \frac{4\pi h^3 \nu^2}{c^3} V. \quad \dots (4)$$

According to the quantum theory, the phase-space can be split up into cells each of volume h^3 , hence the total number of cells

$$= \frac{4\pi h^3 \nu^2}{c^3} V / h^3 = \frac{4\pi \nu^2}{c^3} V, \text{ or } \frac{8\pi \nu^2}{c^3} V, \quad \dots (5)$$

when we take both the polarized pulses. The number $P = \frac{8\pi \nu^2}{c^3}$ represents the total number of ways in which a quantum $h\nu$ can be contained within unit volume. The idea is therefore the same as the number of stationary waves.

The essential point in the above argument is that the *translatory motion* of a pulse of light can be treated according to the quantum theory, viz., $\int dp_x dp_y dp_z = h$ for any one of the degrees of freedom of the pulse of light.

We can now calculate the entropy of radiation by using the relation

$$\text{Now } W = \{\gamma\} / \{\gamma\}_0, \quad \{\gamma\} = \Pi(\mu) P, \quad \dots (6)$$

where (μ) = phase-space described by one pulse in its internal electromagnetic vibrations, P = permutability of the pulses. We are not yet acquainted with any method for expressing the internal vibrations within a light-pulse in terms of Hamiltonian coordinates. Planck and other authors, e.g. Darwin and Fowler, identify the pulse with some resonator—Hertzian oscillator, or the Bohr-vibrator. But we think it may be possible, in the case of a free pulse, to avoid this appeal to material carriers. At any rate, we assume that the pulse is subject to Hamilton's equation

$$\int \int dp_x dp_y = h,$$

for each of its degrees of vibrations.

$$\text{Then } \Pi(\mu) = h^{3N\nu},$$

which means that the pulses do not interchange energy, like gas-molecules, but are independent of each other.

$$P = \frac{A+N!}{A! N!}, \quad \dots (7)$$

because any one of the cells may contain 0, 1, 2, ... $N\nu$ pulses.

$$\text{Thus } \{\gamma\} = h^{3N\nu} \frac{A+N!}{A! N!} \quad \dots (8)$$

We have now to find out the value of $\{\gamma\}_0$. This brings us to the point: how we can reach the absolute zero by using radiation as the working substance in a Carnot reversible engine as was first done by Bartoli. Wien showed that we can pass from a radiation space at temperature T to a space at temperature T' by a virtual slow displacement of the walls. The wave-lengths of radiation enclosed within the space are changed according to the relation

$$\lambda T = \lambda' T',$$

$$\text{or } \nu = \kappa T.$$

Hence at $T=0$, $\nu=0$, i.e. at absolute zero, it is not possible to have any radiation at all.

This brings us to an interesting analogy. We have seen in the previous paper that if we use a gas as a working substance in the Carnot cycle, absolute zero can be attained only when all matter has been annihilated. The present theorem tells us that if we use radiation as a working substance, absolute zero can be attained in a space where all radiation has been completely annihilated.

We thus obtain $A=0$, $P=1$,

$$\text{and } \{\gamma\}_0 = \Pi(\mu) P = h^{3N\nu}, \quad \dots (9)$$

$$\therefore W = \{\gamma\} / \{\gamma\}_0 = \frac{A+N!}{A! N!}, \quad \dots (10)$$

from which the value of S can be easily deduced.

If we use $A\nu d\nu$, $N\nu d\nu$ instead of A and N , we obtain

$$\text{Probability } W = \frac{(A\nu + N\nu)!}{A\nu! N\nu!}.$$

It is easy to see that this equals

$$\left\{ \frac{(A\nu + N\nu)!}{A\nu! N\nu!} \right\}^{d\nu} \quad \dots (11)$$

or in other words,

$$S_{d\nu} = d\nu \cdot k \log \frac{(A\nu + N\nu)!}{A\nu! N\nu!} \quad \dots (12)$$

$S_{d\nu}$ now denoting entropy of radiation having their frequency between ν and $\nu + d\nu$.

The value of S_{ν} , U_{ν} can be calculated with the aid of the above expression, and the relation $\frac{dS_{\nu}}{dU_{\nu}} = \frac{1}{T}$, but as these calculations are to be found in every standard text-book on radiation, they are not reproduced here.

33. ON THE INFLUENCE OF RADIATION ON IONIZATION EQUILIBRIUM*

MEGHNAD SAHA & RAMANI KANTA SUR

(*Phil. Mag., Sr. VII, 1*, 1025, 1926)

1.

The chief desideratum of the present theories of thermal ionization of gases is that they fail to take any account of the influence of radiation on ionization equilibrium. Yet it can easily be shown, and it has been pointed out by many investigators, that radiation plays an essential role in many physical and astrophysical phenomena. Russell¹ pointed out the possible influence of radiation in the barium-sodium anomaly in the solar photosphere, where barium is found to be almost completely ionized, while sodium is only partially ionized, though both elements possess identical ionization potentials. He traced the phenomena to the fact that Ba^+ -atoms are susceptible to photospheric radiation, because the resonance lines lie at 4934, 4554, while Na^+ -atoms are not so, because their resonance lines probably lie far in the ultra-violet. Milne² points out that radiation pouring out through the solar atmosphere is at a higher temperature than the atmosphere itself, and hence the observed ionization is at least partly due to radiation. It recent years, experiments³ have been done in which comparatively cool vapours of alkalis have been ionized by ultra-violet radiation lying beyond the convergence frequency of the principal series of the element. In such cases, the ionization is a purely radiation effect. To the same class of phenomena belong the familiar absorption experiments of Wood and others, where vapours of metals are illuminated by continuous light. In this case the atoms are not ionized, but as a result of the interaction between matter and radiation the valency electron is lifted to higher orbits. There is, in fact, no essential difference between this class of phenomena and phenomena known as photo-chemical reactions, only in the latter case the unit mechanism of reaction is rather obscure.

The treatment of this class of phenomena from the theoretical side is fraught with several difficulties, viz. (1) the mechanism of absorption of a pulse of light by an atom has not yet been tackled successfully on the quantum-mechanical basis; (2) in a reaction of this type, the reacting pulses do not all have the same frequency, i.e. the absorption lines have a finite breadth. This means that when pulses slightly differing from the resonance lines collide with the atom, there is a probability of their being absorbed, but the value of this probability factor varies from a maximum for the centre of the absorption line to rapidly decreasing values on both sides of the centre. Again, the maximum absorption varies from line to line. Thus Füchtbauer found that for the same intensity D_2 is twice as strongly absorbed as D_1 .

Up to the present time neither the physical basis of fine width of absorption lines has been cleared up, nor are we in possession of any formula for absorption applicable to all the lines of a series.

2.

The attempts which have been made to deal with the interaction between matter and radiation⁴ may be broadly subdivided into two classes—(1) those based on the methods used in the kinetic theory of gases; (2) those based on thermodynamical methods. To the first category belong the works of Milne⁵ "On the Statistical Equilibrium in relation to Photoelectric Effect," and of R. H. Fowler⁶ "On Statistical Equilibrium and the Mechanism of Ionization by Electronic Impacts." In these cases some knowledge or some assumption regarding the details of the unit mechanism of reaction is essential. Milne assumes that high temperature ionization is largely a volume photoelectric phenomenon, while Fowler treats the case where

*Communicated by the Authors.

¹ Russell, *Astrophysical Journal*, lvi. May 1922.

² Milne, in a note to 'Nature', see *Month. Notices R. A. S.* June 1925.

³ Foote & Mohler, *Physical Review*, xxvi. p. 195 (1925).

⁴ See *Month. Notices R. A. S.* lxxxv. June 1925; the controversy between Milne and Stewart.

⁵ Milne, *Phil. Mag.* (6) xlvii. p. 200.

⁶ R. H. Fowler, *Phil. Mag.* (6) xlvii. p. 257.

ionization is promoted by collision, in particular by electronic impacts. It may be mentioned that these methods follow on the lines initiated by Guldberg and Waage, Boltzmann, and J. J. Thomson in dealing with the problems of dissociation equilibrium and molecular aggregation⁷. In the thermodynamical method, as developed by van't Hoff, Nernst, Sackur⁸, and others, a knowledge of the detailed mechanism is not so indispensable.

The result is obtained by a treatment of the initial and final states, provided the net charge in energy-content is known. The theory thereby loses somewhat in definiteness, but it has the compensating advantage of being free from the vagueness of the assumptions involved in the kinetic methods.

In the present paper we have followed Ehrenfest's method of dealing with dissociation equilibrium. Attempts in this direction have already been made by R. H. Fowler⁹, Fowler and Milne¹⁰ and by Becker¹¹. But they confined their attention to the production of metastable states.

Ehrenfest¹² has shown that the behaviour of a mixture of gases in thermodynamical equilibrium can be defined by a function $\{\gamma\}$ which may be regarded as the total phase-space described by the system. The function $\{\gamma\}$ is allied to the familiar entropy function, but Ehrenfest did not trace the connexion between the two. In two previous papers¹³, we have shown that $\{\gamma\}$ is connected with Boltzmann's probability function W , by the relation:

$$W = \{\gamma\} / \{\gamma\}_0,$$

where $\{\gamma\}_0$ = value of $\{\gamma\}$ when the system is reduced to absolute zero of temperature.

This theorem holds not only for matter, but we showed in the second paper that it also holds for radiation. The entropy of radiation can be calculated from formula (1) by an extension of S. N. Bose's method¹⁴.

This is equivalent to treating radiation as a new component in chemical equilibrium. A similar view has already been expressed by Smit; according to him the familiar phase-rule

$$F = C + 2 - P$$

has to be replaced in photochemical reactions by the rule $C + 3 - P$. The photochemically active light plays the role of a new component.

Turning to the present case, it is easy to see that a sodium atom with its electron in the $2p$ -orbits or any higher orbit may be regarded as a chemical entity different from a normal Na-atom. The Na_{2p} atom may, for practical purposes, be regarded as compound of Na-(normal) and D_1, D_2

pulses. Thus the lines of the sodium spectrum, Na^+ -ion and the electron may be regarded as the independent components out of which the whole system, consisting of normal atom Na^+ and the metastable states of Na, are evolved.

3.

Let us now consider a system consisting of

$$\begin{aligned} n_1 & \dots \dots \dots \text{neutral atoms,} \\ n_2 & \dots \dots \dots \text{ionized atoms,} \\ n_3 & \dots \dots \dots \text{free electrons.} \end{aligned}$$

Let $n_1 + n_2 + n_3 = n$, and K = kinetic energy of the material particles. Let $N_\nu d\nu$ = total number of quanta of frequency comprised within the range $d\nu$. Then, according to the methods described in the previous papers,

$$W_{d\nu} \text{ for radiation} = \Pi \left\{ \frac{(A_\nu + N_\nu)!}{(A_\nu! N_\nu!)} \right\} d\nu \quad \dots (1)$$

For the material particles

$$W_p = \frac{\mu_1^{n_1}}{h^{3n_1} n_1!} \cdot \frac{\mu_2^{n_2}}{h^{3n_2} n_2!} \cdot \frac{\mu_3^{n_3}}{h^{3n_3} n_3!} \quad \dots (2)$$

We shall here ignore the motion of an electron about its nucleus, and suppose that each material particle has only three degrees of freedom, viz. those corresponding to the motion of translation along three mutually perpendicular axes. Therefore, we have,

$$\left. \begin{aligned} \mu_1 &= \int \dots dx dy dz \cdot dp_x dp_y dp_z \\ &= V \int \dots dp_x dp_y dp_z \\ \mu_2 &= V \int \dots dp_x' dp_y' dp_z' \\ \mu_3 &= V \int \dots dp_x'' dp_y'' dp_z'' \end{aligned} \right\} \quad \dots (3)$$

V = total volume of the gas, and p_x, p_y, p_z , etc. represent the momenta coordinates of the particles.

Hence

$$W_p = \frac{V^n}{h^{3n} n_1! n_2! n_3!} \int \dots dp_{1x} dp_{1y} dp_{1z} \dots dp_{1x}' dp_{1y}' dp_{1z}' \dots dp_{1x}'' dp_{1y}'' dp_{1z}'',$$

the integrals being taken for all molecules of each class. The total kinetic energy K being given, the integration is to be performed subject to the condition

$$\sum \frac{p_{1x}^2 + p_{1y}^2 + p_{1z}^2}{2M} + \sum \frac{p_{1x}'^2 + p_{1y}'^2 + p_{1z}'^2}{2M} + \sum \frac{p_{1x}''^2 + p_{1y}''^2 + p_{1z}''^2}{2m} = K, \quad \dots (4)$$

where M = mass of a neutral atom and m = mass of an electron.

⁷ For a summary, see Jeans, 'Dynamical Theory of Gases,' chap. 7, 209-219.

⁸ See Sackur, 'Thermodynamics,' chap. 9.

⁹ Fowler, Phil. Mag. (6) xlv. p. 1.

¹⁰ Fowler & Milne, Month. Notices Roy. Ast. Soc. lxxxiii. p. 403.

¹¹ Becker, *Zs. für Physik*, xviii. p. 325.

¹² Ehrenfest & Trkal, *Proc. Amst.* xxi. (1920); *Ann. der Physik*, lxiii.

¹³ Saha & Sur, Phil. Mag. Jan. 1926, p. 279.

¹⁴ S. N. Bose, *Zs. für Physik*, xxvi. p. 178 (1924); xxvii. p. 384.

Thus

$$W_p = \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1! n_2! n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)!} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3} \dots (5)$$

For the total system, consisting of radiation and material particles,

$$W = W_{dv} \cdot W_p,$$

or

$$W = \Pi \left\{ \frac{(A_s + N_s)!}{A_s! N_s!} \right\}^{dv} \cdot \frac{V^n}{h^{3n}} \cdot \frac{1}{n_1! n_2! n_3!} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)!} \cdot (\sqrt{M^3})^{n_1} (\sqrt{M^3})^{n_2} (\sqrt{m^3})^{n_3}. \quad (6)$$

Let us now consider a unit process in which a neutral atom is dissociated into a free electron and a positively charged atom by the absorption of a quantum $h\nu$. Then

$$\begin{array}{lll} n_1 & \text{changes to} & n_1 - 1 \\ n_2 & \text{,, ,} & n_2 + 1 \\ n_3 & \text{,, ,} & n_3 + 1 \\ n & \text{,, ,} & n + 1 \\ N_s dv & \text{,, ,} & N_s dv - 1. \end{array}$$

The total energy E of the combined system, however, remains unaltered, i.e. $dE = 0$,

$$dE = dK + \chi - h\nu = 0,$$

or

$$dK = h\nu - \chi, \quad \dots (7)$$

where χ represents the ionization potential per atom. The probability of the system now is

$$W' = \Pi \frac{(A_s dv + N_s dv - 1)!}{A_s dv! (N_s dv - 1)!} \cdot \frac{V^{n+1}}{h^{3(n+1)}} \cdot \frac{\{2\pi(K + dK)\}^{\frac{3(n+1)}{2}}}{(n_1 - 1)! (n_2 + 1)! (n_3 + 1)!} \cdot \frac{(\sqrt{M^3})^{n_1 - 1} (\sqrt{M^3})^{n_2 + 1} (\sqrt{m^3})^{n_3 + 1}}{\left(\frac{3(n+1)}{2}\right)!} \dots (8)$$

For equilibrium,

$$dW = W' - W = 0, \quad \dots (9)$$

whence we obtain,

$$\frac{1}{n_1} \cdot \frac{A_s dv + N_s dv}{N_s dv} \cdot \frac{(2\pi K)^{\frac{3n}{2}}}{\left(\frac{3n}{2}\right)!} = \frac{V}{h^3} \cdot \frac{1}{n_2 n_3} \cdot \frac{\{2\pi(K + dK)\}^{\frac{3(n+1)}{2}}}{\left(\frac{3(n+1)}{2}\right)!} \cdot m^{3/2}.$$

Replacing $\left(\frac{3n}{2}\right)!$ by $\left(\frac{3n}{2}\right)!$ and using Stirling's formula,

$$\begin{aligned} \frac{n_2 \cdot n_3}{n_1} &= \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{2} \right\}^{3/2} \cdot \left(1 + \frac{dK}{K}\right)^{\frac{3n}{2}}, \\ \frac{n_2 \cdot n_3}{n_1} &= \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot \left\{ \frac{2\pi m K}{2} \right\}^{3/2} \cdot \left(1 + \frac{3n dK}{2K}\right). \quad \dots (11) \end{aligned}$$

Putting $K = \frac{3n}{2} kT$, and using (7), we have, after taking logarithms,

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{h\nu - \chi}{kT} + \log \left\{ \frac{N_s}{A_s + N_s} \cdot \frac{V}{h^3} \cdot (2\pi m kT)^{3/2} \right\}. \quad \dots (12)$$

Now

$$\frac{N_s}{A_s + N_s} = \frac{\rho_v}{8\pi \frac{h\nu^3}{c^3} + \rho_v} \quad \dots (13)$$

Using partial pressures, we have, after some reduction,

$$\begin{aligned} \log \frac{p_2 \cdot p_3}{p_1} &= \frac{N h\nu - U}{RT} + \log \frac{\rho_v}{8\pi \frac{h\nu^3}{c^3} + \rho_v} + \frac{5}{2} \log T \\ &+ \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{3/2}}{h^3} \right\}, \quad \dots (14) \end{aligned}$$

where N = Avogadro number,

U = Ionization potential for a mol.

If the temperature of radiation be the same as that of the gaseous system

$$\rho_v = 8\pi \frac{h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1}, \quad \dots (15)$$

the quantity $\frac{\rho_v}{8\pi \frac{h\nu^3}{c^3} + \rho_v}$ reduces to $e^{-\frac{h\nu}{kT}}$ and the equation

(14) reduces to the familiar form

$$\log \frac{p_2 \cdot p_3}{p_1} = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h} \right\}. \quad \dots (16)$$

If, within the reaction-space, the density of radiation be the same as that given within black-body chamber,

$$\frac{\rho_v}{8\pi \frac{h\nu^3}{c^3} + \rho_v} = e^{-\frac{h\nu}{kT_s}},$$

where T_s = temperature of radiation.

Then

$$\begin{aligned} \log \frac{p_2 \cdot p_3}{p_1} &= \frac{N h\nu}{RT} \left(\frac{1}{T} - \frac{1}{T_s} \right) - \frac{U}{RT} + \frac{5}{2} \log T \\ &+ \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad \dots (17) \end{aligned}$$

This formula is practically identical with one given earlier by Einstein¹⁵. Einstein's formula was deduced from photo-chemical reactions, and runs thus:

$$\log \frac{n_2 \cdot n_3}{n_1} = \frac{Nh\nu}{R} \left(\frac{1}{T} - \frac{1}{T_s} \right) + \frac{1}{R} \Sigma \delta n \left\{ c_v \log T + c_1 - (c_v + R) - \frac{b}{T} \right\}. \quad (17')$$

It is easy to see that we can apply this formula directly to the present case and arrive at (17).

Formula (14) is, however, quite general and can be adapted to the circumstances of the case. In place of ρ_ν we have now to use I_ν , where I_ν is the intensity of light from the source in the reaction-space. The formula then takes the form:

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{Nh\nu - U}{RT} + \log \frac{I_\nu}{2 \frac{h\nu^3}{c^2} + I_\nu} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}.$$

As a special case, let the radiation proceed from a black-body radiator at temperature T_s , and let the radiation confined within a solid angle w . Let F_v be its residual intensity in the reaction-space, i.e. $F_v = r \cdot I_v$, r being a fraction and

$$I_v = 2 \frac{h\nu^3}{c^2} \cdot \frac{1}{e^{\frac{h\nu}{kT_s}} - 1}.$$

The quantity $\frac{\rho_\nu}{8 \frac{h\nu^3}{c^3} + \rho_\nu}$ is to be replaced by $\frac{r \frac{w}{4\pi} \cdot I_v}{2 \frac{h\nu^3}{c^3} + r \frac{w}{4\pi} I_v}$,

or to a first approximation by $r \frac{w}{4\pi} e^{-\frac{h\nu}{kT_s}}$.

The formula (14) then reduces to

$$\log \frac{p_2 \cdot p_3}{p_1} = \frac{Nh\nu - U}{RT} + \log \left(r \frac{w}{4\pi} e^{-\frac{h\nu}{kT_s}} \right) + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right\}. \quad \dots (18')$$

4

Influence of Radiation in producing Higher Quantum States.

By a similar treatment it is possible to deduce the equilibrium between normal and excited states. Let

n_1 = number of atoms in the normal state
(1s in the case of Na, 2p in the case of Al).

n_2 = number in any higher excited state
(2p in the case of Na).

$$n_1 + n_2 = n.$$

$Nd\nu$ = number of energy pulses within the frequency region ν , $\nu + d\nu$. The normal atoms pass to the excited state by the absorption of these pulses.

Then we have

$$W = \left\{ \frac{(A+N)!}{A! N!} \right\}^{dv} \cdot \frac{g_1^{n_1}}{h^{3n_1} \cdot n_1!} \cdot \frac{g_2^{n_2}}{h^{3n_2} \cdot n_2!} \cdot \frac{V^n}{\left(\frac{3n}{2} \right)} \cdot (2\pi K)^{\frac{3n}{2}} \cdot m^{\frac{3n}{2}};$$

g_1 and g_2 represent the statistical weights of the two states, K the total kinetic energy, and m the mass of the atoms.

If we take a virtual displacement (unit change) in which n_1 changes to $n_1 - 1$, n_2 to $n_2 + 1$, and $Nd\nu$ to $Nd\nu - 1$, we have

$$W' = \frac{(Adv + Nd\nu - 1)!}{Adv! (Nd\nu - 1)!} \cdot \frac{g_1^{n_1-1} \cdot g_2^{n_2+1}}{h^{3n_1} \cdot (n_1 - 1)! \cdot (n_2 + 1)!} \cdot \frac{V^n}{\left(\frac{3n}{2} \right)} \cdot \{2\pi K + dK\}^{\frac{3n}{2}} \cdot m^{\frac{3n}{2}},$$

where $dK = h\nu - \chi$; χ now represents the difference in the energy levels of the two states.

Now putting

$$W' - W = 0 \quad \text{and} \quad K = \frac{3n}{2} kT,$$

we have

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{N}{A+N} \cdot \left(1 + \frac{h\nu - \chi}{kT} \right),$$

or $\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{N}{A+N} \cdot e^{\frac{h\nu - \chi}{kT}}$ to an approximation,

$$\text{i.e.} \quad \frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot \frac{\rho_\nu}{8\pi \frac{h\nu^3}{c^3} + \rho_\nu} \cdot e^{\frac{h\nu - \chi}{kT}} \quad \dots (19)$$

When the radiation is in temperature equilibrium with the gas, it is easy to see that

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \cdot e^{-\frac{\chi}{kT}} \quad \dots (20)$$

When T is sufficiently high

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \quad \dots (21)$$

as is apparent from the definition of weight factor.

Conclusion

It will be seen from an inspection of the formulae deduced that the finite breadth of the absorption band does not occur in any one of them. This shows that the formulae can be regarded only as approximate. This is not unexpected, because the idea of absorption is rather foreign to the thermodynamical methods.

After a short note announcing this result was published in 'Nature' (Nature, April 11, 1923), Woltjer published a note in which he mentioned that the formulae (14) and (19) could be obtained from Milne's method of treatment. We have found that this method gives identical results. But contrary to our expectations, even in this method of treatment the absorption factor does not occur.

October 1, 1925.

¹⁵ Einstein, *Ann. der Physik*, xxxvii. p. 838.

34. NITROGEN IN THE SUN

(*Nature*, **117**, 268, 1926)

The occurrence of nitrogen in the sun is still an open question. No familiar lines, for example, $\lambda 3995$, have yet been detected in the Fraunhofer spectrum, but the presence of the element is indicated by the cyanogen bands.

It appears that the difficulty of identifying nitrogen by its line spectrum can be traced to the nature of the spectrum itself. Under the ordinary conditions of excitation, nitrogen gives several classes of band spectra, while lines obtained under a higher stimulus, including $\lambda 3995$, have been assigned by Fowler to N^+ . The arc lines of nitrogen itself are evidently lost between these two stages. Kiess (*Journ. Opt. Soc. Am.*, June 1925) has recently elucidated this point. He finds that the chief lines of nitrogen lie either in the extreme ultra-violet or in the extreme infra-red, so that workers confining themselves to the usual spectroscopic region miss them completely.

Kiess has given, in the paper mentioned above, a provisional classification of the arc lines. The principal lines are in the Schumann region, $\lambda 1742.81$, 1745.31 , etc., ..., but the next strongest group from $\lambda 8656$ to $\lambda 8629$ constitutes a pp' combination. There is another pp' group at $\lambda 8200$, but they come from a higher level. It is interesting to see whether these lines occur in the Fraunhofer spectrum. On examining the excellent photographs of the infra-red spectrum of the sun given by Meggers (*Astro. Journ.*, vol. 47, p. 1), the presence of some of the lines was clearly observed, while the others were found to occur rather faintly. A complete comparison was not possible, as the author had no access to a full list of the wave-lengths of the infra-red solar lines. Miss C. Payne in her recent monograph "On Stellar Atmospheres" does not mention the occurrence of any nitrogen line in the sun or in any low temperature star. The only nitrogen line which can be identified without ambiguity in the stellar sequence is $\lambda 3995$. This, however, does not occur in the sun; it occurs,

according to Payne, first in the A_0 class, and Fowler assigns it to N^+ .

If this identification of the arc lines of nitrogen in the sun is verified, it will enable us to fix with some definiteness the energy of dissociation of N_2 . Some years ago, the present writer calculated from the experimental data of Langmuir that the energy of dissociation of N_2 is of the order of magnitude 1.50×10^5 gm. calories. Recently, Eucken (*Annalen der Chemie*, Band 440, p. 111) has discussed the thermo-chemical data on this point, and he comes to the conclusion that the energy of dissociation of N_2 cannot be less than 4.4×10^5 gm. calories, or thrice the value calculated by the present writer. If this were the case, nitrogen would not be dissociated at all in the sun, and the atomic spectrum cannot occur there. Calculation shows that it would be appreciably dissociated only in the A_0 class. But, as we have already mentioned, these stars show the lines of N^+ , coming from a level ($2s$) higher than the normal. Hence Eucken's calculations seem to be quite beyond the mark.

Eucken finds from the same line of argument that the energy of dissociation of O_2 cannot be less than 4.25×10^5 calories.

If this were true, no atomic oxygen can occur in the sun. But it is well known that Runge has identified the oxygen triplet $\lambda \lambda 7772, 7774, 7775$ in the Fraunhofer spectrum. According to Hopfield, the excitation potential for these lines is from 8 to 9 volts, so that in the sun, oxygen is not only completely dissociated, but also a considerable fraction of O-atoms is brought to a higher level. The argument is, therefore, fairly decisive that in the case of O_2 , Eucken's calculations are very wide of the mark.

Physics Department,
University of Allahabad,
December 26, 1925.

35. ÜBER EINEN EXPERIMENTELLEN NACHWEIS DER THERMISCHEN IONISIERUNG DER ELEMENTE

Von M. N. Saha, N. K. Sur und K. Mazumdar.

(*Zeit. f. Physik.*, **40**, 648, 1927)

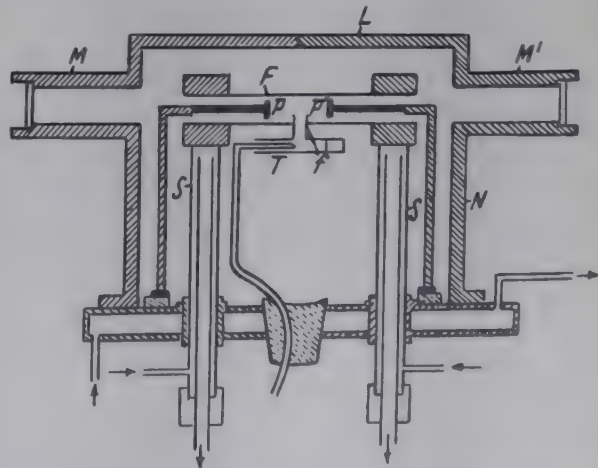
Mit 1 Abbildung. (Eingegangen am 22, November 1926)

Obgleich die Theorie der thermischen Ionisierung der Elemente¹ und ihre Anwendung auf die Astrophysik bereits im Jahre 1920 entwickelt wurde, steht ihre einwandfreie experimentelle Bestätigung noch aus. Im Jahre 1921 wurde von Saha und Günther² im Physikalisch-chemischen Institut der Universität Berlin folgende Untersuchung ausgeführt:

Kleine Stücke von Na, K und Rb wurden in einen von Wasserstoff durchströmten und auf 1250° erhitzten Platinrohrföfen geworfen. Das untere Ende des Ofens war mit Magnesiastücken verschlossen. Die Ionisierung des Alkalidampfraums wurde durch die zwischen der Platinwand und einem innen zentrisch angeordneten Platin-Platinrhodium-Thermoelement (das gleichzeitig zur Temperaturmessung diente) fließenden elektrischen Ströme gemessen. Die angelegte Spannung betrug nur 1 oder 2 Volt, damit die aus der Spaltung des Alkaliatoms in M^+ und e gewonnenen freien Elektronen keine ionisierende Wirkung ausüben konnten. Aber der Spannungsabfall in der Platinröhre selbst, die von durch einen Niederspannungstransformator gelieferten Wechselströmen durchflossen war, betrug mehrere Volt. Man könnte daher leicht den Einwand erheben, dass in einigen Teilen des Dampfraums der wahre Spannungsabfall grösser als die Ionisierungsspannung der Elemente sei, und dass die beobachtete Ionisation nur nach der von Franck und Hertz ausgearbeiteten Methode des Elektronenstosses geschehe. Die Grösse der erhaltenen elektrischen Ströme, die einige Milliampere betrug, sprach indessen entschieden dagegen.

Die nächste Untersuchung³ wurde von Saha und Sur im hiesigen Laboratorium vorgenommen. Der Apparat war ein nach dem Kingschen -Modell gebauter Vakuumofen. Aber die zu untersuchenden Elemente selbst waren in einem zweiten, unter dem ersten angeordneten kleinen Ofen enthalten. Der zweite Ofen war ein mit Chromnickeldraht bewickeltes Quarzrohr und konnte leicht auf 1000°C erhitzt werden. Die Temperatur des Vaku-

umofens, der mit Gleichstrom von einer grossen Akkumulatorenbatterie gespeist wurde, konnte wegen deren schneller Erschöpfung nur einige Minuten auf 1300° gehalten werden. Der zweite Ofen diente zur Feinregulierung der Dampfmenge. In seiner Mitte war der Dampf gesättigt, und wenn die Temperatur bekannt war, konnte der Druck leicht aus einer Dampfdrucktabelle⁴ entnommen werden. Der Dampf im Innern des ersten Ofens war ungesättigt, aber der Druck musste derselbe sein wie im Innern des zweiten Ofens wenn das Ende des ersten Ofens verschlossen war. Die Anordnung gestattete daher eine gleichzeitige Regulierung der Temperatur sowie auch der Konzentration in dem zu untersuchenden Dampfraum. Mit dieser Anordnung konnte die thermische Ionisierung von Alkalien, Ca, Sr und Ba, Zn, Mg bei 1500°C gemessen werden, aber derselbe Einwand, der gegen die frühere Untersuchung erhoben wurde, traf auch hier zu. Wir haben daher einen neuen Apparat gebaut, für welchen nach unserer Meinung die oben erwähnten Einwände durchaus entkräftet sind. Die Anordnung der Öfen ist dieselbe wie vorher, aber die elektrischen Ströme werden zwischen zwei auf Molybdänstäben montierten, gegeneinander und gegen die Öfen isolierten, parallel angeordneten Graphitplatten gemessen. Die Anordnung wird durch die Fig. 1 erläutert.



¹ J. Eggert, *Phys. ZS.* **20**, 570, 1919; M. N. Saha, *ZS. f. Phys.* **6**, 40, 1921; ausführlicher Bericht bei Freundlich, *Handbuch der Physik* XI.

² M. N. Saha und P. Günther, *Journ. of Sc.*, Calcutta University 1922 S. 1—10.

³ M. N. Saha und N. K. Sur, *Journ. Indian. Chem. Society* **1**, 9, 1925.

⁴ Zum Beispiel Landolt-Börnstein, *Physik.-chemische Tabellen*, 5. Aufl., S. 1332 ff., 1923.

Das Graphitrohr F (Länge 10 cm, lichte Weite 14 mm, Wandstärke etwa 2 mm) dient als Vakuumofen. Die Energie wurde von einem Niederspannungstransformator (A. E. G., Berlin) von 10 kW Leistung durch ein von Wasser durchflossenes dickwandiges Eisenrohr (S, S) geliefert. Die Temperatur konnte leicht auf 2000°C gehalten werden. Die Öfen wurden durch einen Eisenmantel geschützt. f ist der kleine, mit Chromnickeldraht bewickelte Quarzofen, der das zu untersuchende Element enthält; T ist das Thermoelement, das zur Temperaturmessung diente. pp' sind die auf Molybdänstäben montierten Graphitplatten; sie sind von F völlig isoliert und befinden sich in kleinem Abstand voneinander, damit der Zwischenraum gleich temperiert war. Die Platten verhindern auch den Dampfausfluss und machen die Konzentration gleichförmig. Die angelegte Spannung war nur 1 Volt, und der elektrische Strom wurde durch ein mit einem Milliampereometer geeichtes Galvanometer gemessen.

L ist der Eisenmantel und MM' Ansatzisenrohre, die mit Quarzfenstern verschlossen waren.

Zur Messung der Temperatur des Vakuumofens während der Versuche diente ein Wannersches Pyrometer, das auf die Quarzfenster gerichtet wurde. Da aber erfahrungsgemäss die von der Seite beobachtete Temperatur um 100 bis 200°C niedriger ist als die wahre Temperatur, wurde nach Kings Vorgang in einem Vorversuch eine der Graphitplatten pp' beseitigt und das Pyrometer auf die andere Platte gerichtet. Dies gibt dann die wahre

Hohlraumtemperatur. Die Unterschiede der zwischen seitlich beobachteten und der wahren Hohlraumtemperatur wurde dann in Abhängigkeit von der Leistung tabelliert und bei den eigentlichen Messungen in Rechnung gezogen.

Der Betrag der Oberflächenemission der Elektronen von pp' wurde folgendermassen ermittelt: Der untere Ofen wurde kalt belassen, damit kein Dampf in den Raum zwischen p und p' eintrat. Der grosse Ofen wurde dann auf etwa 2000°C erhitzt und die beiden Platten abwechselnd positiv und negativ geladen. Der Galvanometerausschlag auf beiden Seiten der Nullage war immer derselbe. Wurde dann eine der Platten aus dem gleichtemperierten inneren Raume in den kälteren äusseren Raum gezogen so schlug, wenn diese kältere Elektrode negativ geladen wurde, das Galvanometer nicht aus.

In der weiteren Untersuchung wurde der untere Ofen mit verschiedenen Elementen beschickt und auf eine passende Temperatur erhitzt. Mit Hg, Zn, Cd wurde kein Galvanometerausschlag erhalten. Mit Mg trat nur ein kleiner Ausschlag auf. Dagegen wurden mit Na und K die Ausschläge sehr gross, und die elektrischen Ströme konnten nur noch mit einem Milliampereometer gemessen werden. Die Temperatur des oberen Ofens wurde abwechselnd auf 1300 bis 2000°C gehalten.

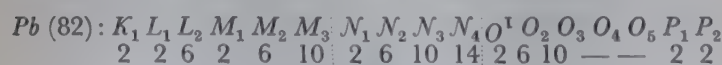
Die Ergebnisse sind völlig im Einklang mit der Grösse der Ionisierungsspannungen der untersuchten Elemente und werden demnächst ausführlicher mitgeteilt werden.

36. ÜBER DAS MAINSMITH-STONERSCHE SCHEMA DES AUFBAUS DER ATOME

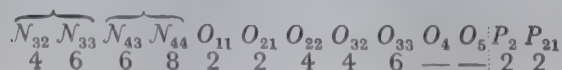
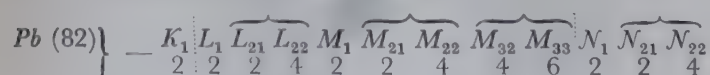
Von M. N. Saha und B. B. Ray

(Physik Zeitschr., 28, 221, 1927)

Bekanntlich haben Main Smith und Stoner das Bohrsche Schema des Aufbaus der Atome dadurch modifiziert, dass sie jedes $L_2, M_2, M_3 \dots$ Niveau in zwei durch verschiedene innere Quantenzahlen j und $j+1$ bezeichnete Unterniveaus spalten. Z. B. für den Aufbau der Atome von Pb kann man nach Bohr schreiben:



Nach Main Smith und Stoner dagegen:



Jedes der oberen L_2, M_2, M_3 usw. Niveaus wird in zwei

Unterniveaus $\overbrace{L_{21} L_{22}}, \overbrace{M_{21} M_{22}}, \overbrace{M_{32} M_{33}}$ gespalten.

Nach Stoner¹ erklärt sein Schema die Entstehung der K -, L -, M -Röntgenspektren viel besser als das Bohrsche Schema. Es erklärt die Existenz zweier verschiedener L -Absorptionskanten $L_{21} L_{22}$, zweier M_2 -Absorptionskanten $M_{21} M_{22}$, zweier M_3 -Absorptionskanten $M_{32} M_{33}$ usw. Nach Stoners und seiner Nachfolger Ansicht war der Ursprung der Emissions-Röntgenstrahlenspektren auch nach der alten Bohrschen Theorie schwer verständlich.

Aber nähere Betrachtungen zeigen, dass das Bohrsche Schema den Ursprung der Emissions- und Absorptions-

¹ Stoner, Phil. Mag. 48, 769, 1924; Sommerfeld, Physik, Zeitschr. 26, 70, 1925.

Röntgenstrahlenspektren mindestens ebenso gut erklären kann wie das Mainsmith-Stonersche, wenn man damit das Paulische Prinzip² der Elektronenbahnen-Synthese koppelt. Schreiben wir z. B. das Bohrsche Strukturdiagramm von Pb in folgender Weise um:

Strukturdiagramm (Pb)

K_1								
2	L_1	L_2						
	2	6 M_1	M_2	M_3				
		2	6 N_1	10 N_2	N_3	N_4		
			2	6 O_1	10 O_2	14 O_3	O_4	O_5
				2	6 P_1	10 P_2	P_3	P_4
					2	(2)		

Die Nummer unter jedem durch grosse Buchstaben bezeichneten Niveau bezeichnet die Gesamtzahl der Elektronen, die nötig sind, um das Niveau vollständig zu besetzen. Diese Art der Darstellung leitet uns zum klaren Verständnis des periodischen Systems, so wie auch zum Verständnis des Ursprungs der optischen Spektren. (Über Näheres siehe verschiedene noch im Druck befindlichen Mitteilungen in Phil Mag.). Das Elektron kann nur um eine ungerade Zahl von Stufen springen. Jede horizontale oder vertikale Verschiebung des Elektrons zählt man als eine Stufe. Z. B. $L_1 \rightarrow K_1$ ist ein zweistufiger Sprung, und ist verboten. $L_2 \rightarrow K_1$ ist ein dreistufiger Sprung, und ist erlaubt. Diese Regel enthält das vollständige Auswahlprinzip, das für optische wie auch für Röntgenspektren ausnahmslos gilt, und alle sogenannten Durchbrechung erklärt.

Die K-Serien erklärt man folgendermassen: Ein Elektron werde durch Elektronenbombardierung von dem K_1 -Niveau entfernt, also es sei nur ein Elektron in K_1 . Ein Elektron wird jetzt von (L_2 , M_2 ... oder jedem durch den Index (2) bezeichneten Diagonalniveau) zu K_1 springen. Den Prozess kann man so veranschaulichen:

$$K_1 \ 6L_2 \rightarrow 2K_1 \ 5L_2$$

$$(L_2 \rightarrow K_1) \text{ gibt uns } K_\alpha, K_{\alpha'}$$

$$K_1 \ 6M_2 \rightarrow 2K_1 \ 5M_2$$

$$(M_2 \rightarrow K_1) \text{ gibt uns } K_\beta, K_{\beta'}$$

Um die zwei verschiedenen Linien K_α $K_{\alpha'}$ zu erklären, ist es nicht nötig, von vornherein das L_2 in L_{21} und L_{22} zu spalten. Nach dem Paulischen Prinzip gibt:

$K_1 \ 6L_2$ eine 2S_1 -Bahn,

[K_1 gibt 2S_1 , $6L_2$ gibt 1S_0 , die resultierende Bahn ist 2S_1]

$2K_1 \ 5L_2$ zwei 2P_1 , 2P_2 -Bahnen

[$2K_1$ gibt 1S_0 , $5L_2$ gibt 2P_1 , 2P_2 , Resultante $^2P_1 \ 2P_2$.

Danach rühren von einem Sprung eines Elektrons von $L_2 \rightarrow K_1$ zwei Linien her:

$$\begin{array}{c|c} & ^2P_1 \ ^2P_2 \\ \hline ^2S_1 & 1 : 2 \\ & (K_{\alpha'}) \ (K_\alpha) \end{array}$$

Das Intensitätsverhältnis folgt aus der Ornstein-Sommerfeldschen Regel.

Das Wesentliche in dieser Betrachtung ist die Tatsache, dass es ganz unnötig ist, das L_2 -Niveau von vornherein als in zwei Unterniveaus gespalten anzusehen. Es gibt nur ein L -Niveau, das sechs Elektronen enthält. Wenn ein Elektron davon entfernt wird, werden nach dem Paulischen Reziprozitätsgesetze die zurückbleibenden fünf Elektronen entweder eine resultierende 2P_1 -oder 2P_2 -Bahn geben. Aber die Spaltung ist dynamisch, nicht statisch, wie von Mainsmith-Stoner angenommen wurde. In jedem normalen Atome gibt es keine von vornherein festgelegte L_{21} L_{22} -Unterniveaus; wenn man aber eine grosse Zahl von Atomen betrachtet, in deren jedem ein Elektron aus dem L_2 -Ring entfernt wird, werden in einem Augenblick bei einem Drittel der Atome die $5L_2$ -Elektronen im 2P_1 -Zustand, bei zwei Dritteln aber im 2P_2 -Zustand sein. Daher ist die Energie des Atomrests für ein Drittel $A-h$ (2P_1), für zwei Drittel $A-h$ (2P_2).

In derselben Weise kann man auch die Absorptionsskante und den Ursprung der L -Reihe erklären. Z. B.: Nehmen wir das L -Spektrum des Wolframs, das am genauesten studiert ist.

Die 2S - $^2P_{1,2}$ -Serie.

$$L_1 \ 6M_2 \rightarrow 2L_1 \ 5M_2 = ^2S_1 - a^2P_{1,2} = 893,0 - 191,3$$

$$= 701,7 \ (\beta_4)$$

$$(M_2 \rightarrow L_1) \quad -169,8 = 723,2 \ (\beta_3)$$

$$L_1 \ 6N_2 \rightarrow 2L_1 \ 5N_2 = ^2S_1 - b^2P_{1,2} = 893,0 - 38 = 855 \ (\gamma_2)$$

$$(N_2 \rightarrow L_1) \quad -33,0 = 860 \ (\gamma_4)$$

Das ($L_1 \ 6M_2$) und ($L_1 \ 6N_2$) bedeutet denselben Zustand, da nur ein Platz im L_1 -Ring leer ist. $b^2P_{1,2}$, dem ($2L_1 \ 5N_2$)-Zustand entsprechend, ist eine Art höherer Rydberg-Term zu $^2P_{1,2}$ des $2L_1 \ 5M_2$ -Zustands.

$$L_1 \ 6N_2 \rightarrow 2L_1 \ 5N_2 = ^2S_1 - c^2P_{1,2} = 893 - 5 = 887,8 \ (\gamma_4)$$

Die $^2P_{1,2}$ - $^2D_{2,3}$ -Serie.

$$5L_2 \ 10M_3 \rightarrow 6L_2 \ 9M_3 = ^2P_{1,2} - a^2D_{2,3}$$

$$= 850,6 - 138,3 = 712,3 \ (\beta_1) \ (^2P_1 - ^2D_2)$$

$$= 752,1 - 138,3 = 613,8 \ (\alpha_2)$$

$$= 752,1 - 133,7 = 618,45 \ (\alpha_1)$$

² Pauli, Zeitschr. f. Phys. 31, 765, 1925.

Nach der Sommerfeld-Ornsteinschen Regel sind die Intensitätsverhältnisse $\beta_1:\alpha_2:\alpha_1=5:1:9$.
 $5L_2.10N_3 \rightarrow 6L_2.9N_3$ gibt ${}^2P_1 - b^2D_2 = 850,6 - 18,8 = 831,8$ (γ_1)
 $N_3 \rightarrow L_2$ ${}^2P_2 - b^2D_3 = 752,1 - 18,4 = 733,7$ (β_2)

Die schwache Linie, ${}^2P_2 - {}^2D_2$ ist von β_2 untrennbar;
 $(O_3 \rightarrow O_2)$ gibt γ_6 und β_5 .

Die ${}^2P_{1,2} - {}^2S_1$ -Serie.

$5L_2.2M_1 \rightarrow 6L_2.M_1$ gibt ${}^2P_{1,2} - b^2S_1 = 850,6 - 208,1 = 642,5$ (η)
 $(L_2 \rightarrow M_1)$ $752,1 - 208,1 = 544,0$ (ϵ).

Diese 2S_1 entsteht durch Entfernung eines Elektrons aus dem M_1 -Ring.

$5L_2.2N_1 \rightarrow 6L_2.N_1$ gibt $({}^2P_{1,2} - c^2S)$ $850,6 - 43 = 807$ (γ_5)
 $(N_1 \rightarrow L_2)$ $752,1 - 43 = 708$ (β_6)

$5L_2.2O_1 \rightarrow 6L_2.O_1$ $({}^2P_{1,2} - d^2S_1)$ $850,6 - 5,7 = 844,5$ (γ_8)³
 $746,4$ (β_7)

Die anderen beobachteten Linien, z. B. β_9, β_{10} entsprechen den optischen Linien ${}^2S_1 - {}^2D_{2,3}$ und durchbrechen die Auswahlregel, ebenso die Dauvillierschen Linien t und s , denen die Sprünge $a^2S_1 - b^2S_1 \dots$ entsprechen.

Wir werden jetzt zeigen, dass das Mainsmith-Stonersche Schema der Spaltung nicht nur unnötig, sondern etwas irreführend ist. Um diesen Punkt zu illustrieren, betrachten wir z. B. die optischen Spektre der Elemente von der dritten und vierten Gruppe.

Das Strukturdiagramm des Aluminiums sei:

K				
2				
	L_1	L_2		
	2	6		
		M_1	M_2	M_3
		2	1	
			N_1	N_2

Im normalen Zustand ist das strahlende Elektron in M_2 , also ist die normale Bahn 2P_1 (M_{21}), oder 2P_2 (M_{22}). Nach der Serienanalyse ist ${}^2P_1 = 48\ 281$, ${}^2P_2 = 48\ 169^4$, und es besteht kein grosser Unterschied zwischen ihrem Energieinhalt. Beide Bahnen sind nach ihrem Energieinhalt gleich wahrscheinlich, nach ihrer inneren Quantenzahl ist 2P_2 zweimal wahrscheinlicher als 2P_1 ; also wenn man eine grosse Anzahl von Atomen nimmt, wird in einem gegebenen Augenblick ein Drittel von ihnen in 2P_1 -Bahnen, zwei Drittel in 2P_2 -Bahnen sein. Nach Mainsmith-Stoner muss man alles in 2P_1 -Bahnen annehmen.

Fassen wir nun das Si-Spektrum ins Auge⁵. Das Si-Atom hat dieselbe Struktur wie Al. Wenn man durch Aufbringen eines neuen Elektrons das Si-Atom völlig aufbaut, besitzt dieses entweder die 2P_1 -oder 2P_2 -Bahn. Man kann nicht sagen, wie nach Mainsmith-Stoner zu erwarten sei, dass die beiden äusseren Elektronen ein mit L_{21} , bezeichnetes

Unterniveau füllen müssen, also die 2P_1 -Bahn besässen. Wenn das geschieht, muss die resultierende Bahn 3P_0 sein, aber nach der Serienanalyse sind neben 3P_0 auch tiefliegende 3P_1 , 3P_2 , 1D_2 , 1S_0 -Bahnen bekannt, und 3P_1 , 3P_2 haben ungefähr denselben Energieinhalt wie 3P_0 . Die Existenz dieser Terme kann man erklären, wenn man annimmt, dass abgesehen von ihren inneren Quantenzahlen die Wahrscheinlichkeit für das Bleiben beider äusserer Elektronen in 2P_1 oder 2P_2 dieselbe ist; man kann leicht zeigen:

${}^2P_1\ {}^2P_1$ (Beide Elektronen in 2P_1 -Bahn) gibt resultierende Bahnen mit $j=0, 1$,

${}^2P_1\ {}^2P_2$ (eins in 2P_1 , das andere in 2P_2) gibt Bahnen mit $j=1, 2$,

${}^2P_2\ {}^2P_1$ gibt Bahnen mit $j=1, 2$,

${}^2P_2\ {}^2P_2$ gibt Bahnen mit $j=0, 1, 2, 3$.

Einige dieser Bahnen sind nach dem Paulischen Prinzip verboten, man erhält nur:

3P_0 , 3P_1 , 3P_2 , 1D_2 , 1S_0 .

Wesentlich zu beachten ist, dass beide Elektronen nach Wahrscheinlichkeitsgesetzen in 2P_1 , 2P_2 -Zustände verteilt sind. Es gibt keine festen Unterniveaus L_{21} mit zwei Elektronen.

Für die Erklärung der tiefliegenden (normalen) Terme anderer Elemente, besonders der ersten grossen Periode braucht man nicht eine feste Spaltung der äusseren M_3 in zwei durch M_{33} , M_{33} bezeichnete Unterniveaus anzunehmen. Schreiben wir zur Illustration das Strukturdiagramm verschiedener Elemente der ersten grossen Periode:

K_1				
2				
	L_1	L_2		
	2	6		
		M_1	M_2	M_3
		2	6	x
			N_1	N_2
			N_3	
			y	
			$y=1$, oder 2,	
			$x=1$, bis 10.	

Elemente	Kombination, die tiefliegende Terme gibt	Tiefliegende Terme
21 Sc	$M_3, 2N_1$	2D
22 Ti	$2M_3, 2N_1$	3F
23 V	$3M_3, 2N_1$	4F
24 Cr	$\{4M_3, 2N_1$	5D
	$\{5M_3, N_1$	7S
25 Mn	$\{5M_3, 2N_1$	6S
	$\{6M_3, N_1$	8D
	$\{6M_3, 2N_1$	5D
26 Fe	$\{7M_3, N_1$	${}^5F, {}^3F$
	$\{7M_3, 2N_1$	4F
27 Co	$\{8M_3, N_1$	4F
	$\{8M_3, 2N_1$	${}^3F, {}^3P, \bar{G}(?)$
28 Ni	$\{9M_3, N_1$	${}^1P, {}^1S_0$
	$\{9M_3, 2N_1$	${}^3D, {}^1D$
29 Cu	$\{10M_3, N_1$	2S_1
	$\{9M_3, 2N_1$	${}^2D_{2,3}$

³ Diese Zahlen wurden den Siegbahnschen "Röntgenstrahlen" entnommen.

⁴ Siehe Fowlers Report on Series Spectra.

⁵ Hund, Zeitschr. f. Phys. 33, 345, 1925; 34, 296, 1925.

Also die Verteilung der M_3 -Elektronen erst in ein vollbesetztes M_{32} -Unterniveau, und dann des Restes in M_{33} ist ganz willkürlich. Nach der erfolgreichen Hundschen Theorie gewinnt man die optisch beobachteten tiefliegenden Terme, wenn man jedem M_3 -Elektron die ${}^2D_{2,3}$ -Bahn zuschreibt, und nach dem Paulischen Gesetz diese kombiniert. Es ist keine Rede von Spaltung: Einige Elektronen in M_{32} , der Rest in M_{33} .

Zur Erklärung der Funkenlinien in Röntgen spektren eröffnet diese Gedankenreihe einen neuen Weg. Bekanntlich hat Wentzel⁶ versucht, die K -Funkspektren von Al und Mg durch gleichzeitiges Entfernen zweier Elektronen aus dem K_1 -Ring zu erklären, aber mit geringem Erfolg. Nehmen wir an, dass die Elektronenbombardierung so geschieht, dass ein Elektron aus K_1 , ein anderes aus L_1 gleich zeitig entfernt werden. Man erhält dann diese Elektronengruppierung:

$K_1 5L_2$ als Anfangszustand, also ${}^3P_{0,1,2}$ 1P_1 -Bahnen (K_1 gibt 2S_1 , $5L_2$ gibt ${}^2P_{1,2}$, die resultierende Bahn ist ${}^3P_{0,1,2}$ 1P_1).

Nun lassen wir ein Elektron aus dem L_2 -Ring zu K_1 springen. Man erhält die Elektronengruppierung:

$2K_1 4L_2$ als Endzustand, also ${}^3P_{0,1,2}$ 1D_2 , 1S_0 -Bahnen.

Der Übergang:

$$K_1 5L_2 \rightarrow 2K_1 4L_2 \\ (\bar{L}_2 \rightarrow K_1).$$

ist erlaubt. Daher kann man die zwei Reihenvon Triplett- p -Termen miteinander kombinieren und wenn die eine Reihen als normal betrachtet wird, muss die andere Reihe gestrichen werden. Man kann jetzt die folgenden Linien erwarteter

	3P_0	3P_1	3P_2	1D_2	1S_0
3P_0		9			
3P_1	9	18— u	u	(15)	(3)
3P_1		u	45— u	(25)	
1P_1	(3)	(9)	(15)	(15)	(3)

⁶ Wentzel, Zeitschr. f. Phys. **31**, 445, 1925.

Die Entstehungsweise ist ganz analog der Entstehungsweise der PP -Multipletten in Spektren von Al , Zn , Cd , Si^{+7} . Die Zahlen bedeuten die erwartete Intensität nach der Ornstein-Sommerfeldschen Regel. Es gibt auch andere Möglichkeiten, aber die letztere scheint die wahrscheinlichste zu sein. Die mit u' bezeichneten Linien sind immer die schwächsten, und die unter und neben dem Triplett-schema liegenden Linien werden erfahrungsgemäss auch sehr schwach sein.

Bei diesem Prozess handelt es sich um die gleichzeitige Entfernung eines Elektrons aus K_1 , und des zweiten aus L_2 . Die Anregungsenergie kann daher die der K -Reihen nicht weit überschreiten, also ungefähr $K_1 + xL_2$, $K_1 = \text{An-regungsenergie für das } K\text{-Spektrum}$, x eine von 1 nicht weit entfernte Zahl, L_2 dieselbe für das L_2 -Spektrum. Die Anregungsenergie für das Entfernen zweier Elektronen aus L_2 ist auch für schwere Elemente etwa zweimal grösser als L_2 , für leichte Elemente kann sie L_2 drei- oder viermal überschreiten.

Für schwere Elemente können daher die Funkenlinien nur mit Schwierigkeit von K -Linien getrennt werden, also als Satelliten zu K -Linien erscheinen, für leichte Elemente dagegen ist die Trennung beobachtbar. Es ist auch nicht nötig, für die verschiedenen Linien weit entfernte Anregungsenergie anzunehmen. Sie gehören zu derselben Multiplettgruppe, und mit zunehmender Stromdichte werden sie immer intensiver. Die Anschauung stimmt mit den Ergebnissen der wichtigsten Versuche von Bäcklin und Larson⁸) über die Anregungsspannung von Funkenlinien, so wie auch mit dem Ergebnis, dass die Intensitätsverhältnisse zwischen Funkenlinien immer dieselben sind.

Allahabad und Kalcutta (Indien)

(Eingegangen 13. Dezember 1926).

⁷ Siehe Saha und Kichlu, Über die anomalen Terme in Erdalkalispektren; wird in Phil. Mag. erscheinen.

⁸ Bäcklin u. Larson.—Siegbahn, Röntgenstrahlen.

37. ÜBER EIN NEUES SCHEMA FÜR DEN ATOMAUFBAU

(Physik Zeitschr, **28**, 469, 1127)

In einer in dieser Zeitschrift¹ vor kurzem erschienenen Arbeit haben B. B. Ray und der Verfasser die Meinung geäußert, dass die Main-Smith-Stonersche Praxis der Unterniveauspaltung (z. B. M_3 in M_{32} , M_{33} ...) nicht nur unnötig, sondern auch irreführend ist. In der Tat gibt es nur:

1. K -Niveau
2. L - „ „ bzw. L_1, L_2
3. M - „ „ „ M_1, M_2, M_3
4. N - „ „ „ N_1, N_2, N_3, N_4

¹ M. N. Saha und B. B. Ray, Physik. Zeitschr., **28**, 221, 1927.

Die Unterniveauspaltung, die zur Erklärung der Röntgenstrahlenspektren nötig erscheint, ist nur scheinbar; es gibt keine statische Spaltung, nur eine dynamische. Es sei noch bemerkt, dass in seiner erfolgreichen Erklärungsweise der Komplexspektren Hr. Hund² keinen Gebrauch von dieser künstlichen Spaltung gemacht hat.

Die in dieser Arbeit entwickelte Gedankenreihe verfolgend, wurde ein neues Schema für den Atomaufbau ausgearbeitet, das eine klare und einheitliche Übersicht

² Hund, Zeitschr. f. Physik, **33**, 345, 1925; **34**, 296, 1925.

über das ganze Gebiet bzw. den Ursprung der optischen und der Röntgenstrahlspektren und die periodischen Eigenschaften der Atome ermöglicht. Es wird kein neues Prinzip entwickelt, aber die früher entdeckten Prinzipien werden in einer neuen graphischen Form dargestellt.

Erklärung zu Fig. 1:

I. K , L , M , bedeuten die nacheinanderfolgenden inneren Niveaus, in welchen die Elektronen verteilt werden. Nach dem Paulischen Prinzip³ haben die Elektronen unter X_1 ($X=K, L, \dots$) die quantenmechanischen Charakteristiken eines Dublett S -Terms ($^2S_{1/2}$), die Elektronen unter X_2 ($X=L, M, \dots$) die Charakteristiken von Dublett- P -Termen ($^2P_{1/2, 3/2}$). Nach Bohr kann man schreiben

K_1	als	$1s$
L_1	„	$2s$
L_2	„	$2p$
M_1	„	$3s$
M_2	„	$3p$
M_3	„	$3d$

Die für die vollständige Besetzung eines jeden Niveaus nötige Zahl. von Elektronen wird aus dem Paulischen Prinzip erhalten, und unter das entsprechende Niveau geschrieben. Es ist 2 für X_1 ($X=K, L, \dots$) 6 für X_2 ($X=L, M, \dots$) 10 für X_3 ($X=M, N, \dots$) 14 für X_4 ($X=N, O, \dots$)

II. Die Energiewerte der Elektronen in verschiedenen Niveaus.

Der Energiebetrag, der nötig ist, um ein Elektron aus einem bestimmten Niveau ins Unendliche zu entfernen, ist aus Röntgenstrahlendaten bekannt. Sei ' v_n ' die

³ Pauli, Zeitschr. f. Physik. 31. 795, 1924.

K_1		Übergangsgruppe I		Übergangsgruppe II	Seltene Erden	Übergangsgruppe III
1 H 2 He	2	21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni	29 Y 30 Zr 31 Nb 32 Mo 33 Tc 34 Ru 35 Rh 36 Pd	37 La 38 Ce 39 Pr 40 Nd 41 Pm 42 Sm 43 Eu 44 Gd 45 Tb 46 Dy 47 Ho 48 Er 49 Tm 50 Yb	71 Lu 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt	89 Ac 90 91 Pa 92 U
3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne	L_1 L_2 L_3 L_4 L_5 L_6 L_7 L_8	11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar	19 K 20 Ca	21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni	29 Y 30 Zr 31 Nb 32 Mo 33 Tc 34 Ru 35 Rh 36 Pd	37 La 38 Ce 39 Pr 40 Nd 41 Pm 42 Sm 43 Eu 44 Gd 45 Tb 46 Dy 47 Ho 48 Er 49 Tm 50 Yb
	M_1 2	M_2 6	M_3 10			
		N_1 2	N_2 6	N_3 10	N_4 14	
			O_1 2	O_2 6	O_3 10	O_4 14
				P_1 2	P_2 6	P_3 10
					Q_1 2	Q_2 6

Fig. 1

charakteristische Frequenz dividiert durch R (Rydbergsche Zahl). Wir haben

$$\begin{array}{c}
 \nu_{K_1} \\
 \nu_{L_1} > \nu_{L_2} \\
 \vee \\
 \nu_{M_1} > \nu_{M_2} > \nu_{M_3} \\
 \vee \\
 \nu_{N_1} > \nu_{N_2} > \nu_{N_3} > \nu_{N_4} \\
 \vee \\
 \nu_{O_1} > \nu_{O_2} > \nu_{O_3} \\
 \vee \\
 \nu_{P_1} > \nu_{P_2}
 \end{array}$$

Wenn wir in Siegbahns⁴ Kurve der Energiebeträge für die einzelnen Röntgenstrahlenniveaus die Energiewerte von Term paaren wie (M_3N_1) , (N_3O_1) , (O_3P_1) vergleichen, welche in Fig. 1 einander diagonal gegenüberliegen, so finden wir, dass sich in ihrem unteren Verlauf die Kurven z. B. für M_3 und N_1 schneiden, also sind ihre Energiebeträge von der gleichen Grössenordnung, dies gilt für Elemente, für welche das M_3 -Niveau anfängt erfüllt zu sein. Daher ist die Wahrscheinlichkeit der Aufnahme des letzten Elektrons in N_1 oder in M_3 ganz gleich.

Durch das Schema wird der Elektronenaufbau der nacheinanderfolgenden Elemente sowie die Struktur der äusseren Niveaus eines jeden Elements veranschaulicht.

Die hier gegebene Struktur wird durch optische Daten bestätigt.

Es sei bemerkt, dass nach dem Schema die ersten Elemente ... H und He etwas abgesondert sind. Dieser Unterschied verschwindet, aber, wenn wir nach Schrödingers Wellenmechanik annehmen dass jede vollständige Schale im dreidimensionalen Atomraum ein kugelsymmetrisches Feld erzeugt.

1. Die regulären Gruppen: Diese bestehen aus Gruppe

1.	3	<i>Li</i>	.	.	.	10	<i>Ne</i>
2.	11	<i>Na</i>	.	.	.	18	<i>Ar</i>
3.	29	<i>Cu</i>	.	.	.	36	<i>Kr</i>
4.	47	<i>Ag</i>	.	.	.	54	<i>Xe</i>
5.	79	<i>Au</i>	.	.	.	86	<i>Nt</i>

Die chemischen und optischen Eigenschaften hängen vollständig von der äusseren Struktur der Elektronenschale ab. In den verschiedenen Gruppen wiederholt sich die Struktur. Jede Gruppe beginnt mit einem Elektron in L_1 (z. B. in Li) und hört mit der Zusammensetzung $(2X_1 6X_2)$ -Elektronen mit einem Elemente von der Valenz 0 auf. Ausführlicher:

1. Li , Na , Cu , Ag , Au ... nur ein Elektron in X_1 (das äusserste Niveau). Sie sind einwertig (Cu und Au bilden eine später zu erklärende Ausnahme).

2. Be , Mg , Zn , Cd , Hg haben zwei Elektronen in X_1 . Sie sind zweiwertig.

3. B , Al , Ga , In , Th ... haben die äussere Struktur $2X_1 X_2$... Sie sind dreiwertig, da X_1 und X_2 ungefähr dieselben Energiewerte haben.

[Diese Annahme wird durch optische Daten bestätigt. Die Kombination $(X_1 2X_2)$ kommt häufig in optischen Spektren vor.]⁵

4. C , Si , Ge , Sn , Pb ... haben die äussere Struktur $(2X_1 2X_2)$... Sie sind vierwertig⁶.

Die Kombination $X_1 3X_2$ wurde von Bowen im C -Spektrum entdeckt. Vgl. Phys. Rev. **29**, 231, 1927. Das bestätigt die aus chemischen Beobachtungen gezogene Folgerung, dass die X_1 -Elektronen zur chemischen Valenz beitragen können.

5. Für Elemente mit der Valenz 0 ist die äussere Struktur $2X_1 6X_2$. Wir kommen später zur Erläuterung ihrer Eigenschaften.

II. Die Übergangselemente (Transitionale Gruppe). Fassen wir nun den Aufbau der Elemente K und Ca ins Auge. Sie haben den Elektronenaufbau

$$\begin{array}{l}
 19K \dots 2K_1 8L 2M_1 6M_1 \dots N_1 \} \\
 20Ca \dots 2K 8L 2M_1 6M_2 \dots 2N_1 \}
 \end{array}$$

Es gibt kein Elektron in M_3 . Die Elemente sind ein- und zweiwertig. Wenn wir das nächste Element, d. h. das Sc -Atom aufbauen, so tritt ein neuer Umstand hervor. Wenn wir Fig. 1 betrachten, so finden wir jetzt ein M_3 -Niveau, welches diagonal zu N_1 liegt, und das den Energiebetrag von N_2 überschreitet. Daher befindet sich das neue Elektron in M_3 , also ist die äussere Struktur $(M_3 2N_1)$. Die optische Analyse fügt dazu eine gleichwahrscheinliche Struktur $2M_3 N_1$. Wir haben daher für Sc :

$$21Sc \dots \text{äussere Struktur} \dots M_3 2N_1 \quad 2M_3 N_1$$

Die maximale Elektronenkapazität des M_3 -niveaus ist 10, und daher wird kein neues Elektron zu N_2 übergehen, bevor M_3 völlig besetzt ist. Wir haben daher acht Übergangselemente mit der äusseren Struktur

$$\begin{array}{c}
 x M_3 N_1 \\
 (x_1) M_3 2N_1
 \end{array}$$

Beide Strukturen sind nach der optischen Analyse gleich wahrscheinlich; Nickel z. B. bildet das letzte Übergangselement mit den Strukturen

$$\begin{array}{c}
 8M_3 2N_1 \dots \\
 9M_3 N_1
 \end{array}$$

Die Übergangstendenz bleibt noch im Kupfer bestehen, das nach optischer Analyse neben der normalen $10M_3 N_1$ eine metastabile $9M_3 N_1$ Struktur⁷ zeigt. Diese liegt ungefähr 1,3 Volt höher als $10M_3 N_1$.

⁵ Siegbahn, loc. cit. S. 198, Fig. 89 u. 90 (englische Ausgabe. Fig. 90b, S. 201).

⁶ Vgl. P. K. Kichlu, Über die Spektren des ionisierten Siliziums. Journ. Opt. Soc. Amerika (im Druck).

⁷ Vgl. Shenstone, Phys. Rev. **28**, 449, 1926; Sommer, Zeitschr. f. Phys. **39**, 711, 1926.

⁴ Siegbahn, The Spectroscopy of X-rays, S. 184. L_3 in Siegbahn bedeutet L_1 hier, L_1 bedeutet L_{31} , L_{32} .

Der Ursprung optischer Spektren

Um den Charakter der optischen Spektren zu bestimmen, schreibt man das volle Strukturdiagramm, d. h. man schreibt $K_1 L_1 L_2 \dots$ in ganz derselben Weise stufenartig nacheinander wie in Schema I, und schreibt unter jedes Niveau die nötige Zahl der Elektronen. Die Reihe erreicht ihr Ende, wenn die Summe die Atomzahl des betreffenden Elements erreicht, für Mg und Ca z. B. haben wir das Schema:

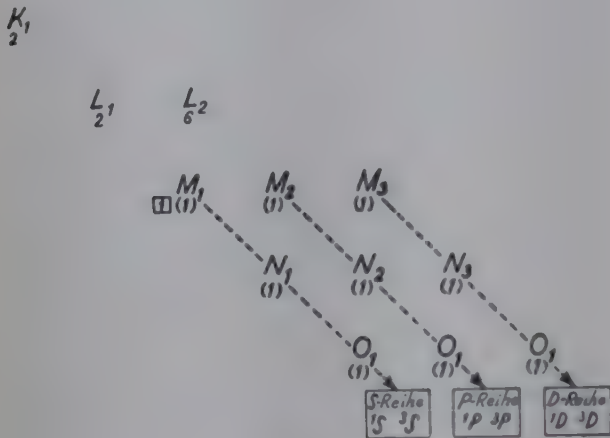


Fig. 2

In Mg hört man bei M_1 auf, in Ca bei N_1 . Jedes enthält zwei Elektronen in X_1 ($X=M$ und N). Nun halten wir ein Elektron in X_1 fest, und lassen das andere durch das höhere, leere Niveau laufen. Der normale Zustand (zwei Elektronen in X_1) gibt uns die tiefliegenden Terme, also $1S_0$. Das festgehaltene Elektron in M_1 und das laufende Elektron in X_2 (X jedes beliebige höhere Niveau), wenn deren quantenmechanische Eigenschaften addiert werden, geben uns die höheren optischen Terme. Alle durch Diagonal-verschiebung des laufenden Elektrons erhaltenen Terme, wenn diese dieselbe Quantencharakteristik besitzen, bilden eine Rydberg-Reihe. Dieser Prozess wird in Fig. 2 und 3 veranschaulicht.

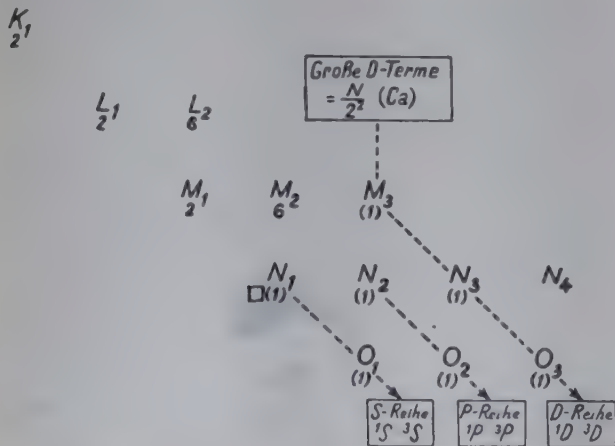
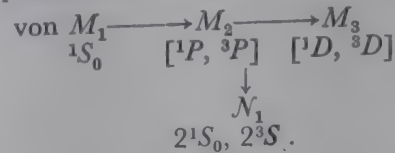


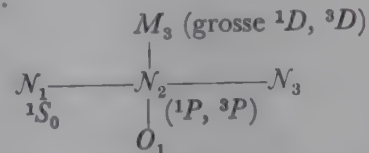
Fig. 3

Nun verfolgen wir den Lauf des optischen Elektrons durch die höheren Niveaus in beiden Figuren. Es tritt eine hauptsächlichliche Differenz hervor. In Mg läuft das Elektron



$1P$ ist ungefähr $\frac{R}{2^2}$, $1D$ ist ca. $\frac{R}{3^2}$

Dagegen in Ca :



also: In Ca gibt es ein leeres M_3 -Niveau, das im Energiewert das N_3 überschreitet, daher gibt $N_1 M_3 \dots$ einen $1D^3D$ -Term, der im Energiewert mindestens einem $N_1 N_2$ -Term gleichkommt. Also ist das erste D -Term ungefähr $= N/2^2$, und nicht $\frac{N}{3^2}$ wie in Mg .

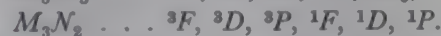
Der grosse D -Term, den man auch als metastabil bezeichnen kann, bildet die Charakteristik des Spektrums für Ca (und mutatis mutandis für Sr und Ba).

Der Ursprung anomaler Terme. Wenn wir ein Elektron in M_3 festhalten und lassen das andere durch das höhere Niveau laufen, so erhalten wir die von Russell und Saunders entdeckten anomalen Terme.

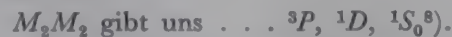
In Ca (Sr und Ba) gibt:



(die früher erwähnten Terme, also sind sie halbanomal)



Anomale Terme in Mg . Es gibt aber anomale Terme auch in Mg und diese erhält man, wenn ein Elektron in M_2 festgehalten wird und das andere durch das höhere Niveau läuft



Diese Idee findet ganz allgemeine Anwendung. Die Gedankenreihe verfolgend, hat Dr. N. K. Sur in Spektren der Übergangselemente, besonders in Co , Rydbergsequenzen gefunden.

Die Übergangsregel. Diese ist ganz einfach. Das Valenzelektron kann nur um eine ungerade Zahl von Niveaus springen, z. B. von L_1 zu L_2 (ein), M_2 (drei), N_3 (fünf). Geradzahlige Sprünge werden verboten. Diese Regel enthält auch die optische Auswahlregel: Kombinationen zwischen solchen Termen sind möglich, welche der Übergangsregel und der Regel für die innere Quantenzahl gehorchen.

Gang der Ionisierungsspannung. Die Ionisierungsspannung hängt von der äusseren Struktur der Atome ab,

⁸ Siehe Kichlu u. Saha, Über anomale Terme der zweiwertigen Atome. Phil. Mag. (July, 1927).

und wird in Kurve I veranschaulicht. Herr R. N. Ghosh hat im hiesigen Laboratorium die Abhängigkeit der Ionisierungsspannungen von der äusseren Struktur ausführlich studiert und er kommt zum Schlusse, dass sie mit zunehmender Anzahl der Gruppen-Elektronen immer zunehmen. Wenn ein Niveau ganz besetzt ist, erreicht die Ionisierungsspannung ein Maximum. Wenn es eine statische M_{32} M_{33} -Spaltung gibt, muss die Ionisierungsspannung bei Erfüllung der M_{32} -Niveau, also bei *Cr* oder *Mn*, ein Maximum erreichen. Zur Illustration fügen wir die folgende Kurve bei, die der Arbeit von R. N. Ghosh entnommen ist.

Es erhellt aus dieser Kurve, dass für Elemente wie *O* und *Fl*, für welche das Niveau ungefähr voll besetzt ist, die Ionisierungsspannung sehr gross ist; und diese Elemente nehmen teichter ein oder zwei neue Elektronen auf, als dass sie eines abgeben. Sie haben die negativen Valenzen zwei und eins. Zu positiver Valenz sind sie unfähig. Bei *Ne* ist die Schale ganz erfüllt, also es ist sehr schwer von *Ne* ein Elektron abzureissen oder anzuregen, und noch schwerer, ein neues Elektron dort anzuheften. Es ist weder zu positiver noch auch zu negativer Valenz fähig.

In allen Elementen, von *B* bis *Fl*, haben wir optische Terme, die zur Kombination

$$L_1(x+1)L_2 \text{ (normal } 2L_1xL_2\text{)}$$

gehören. Das L_1 -Elektron kann leicht zu L_2 übergehen.

Übergangsgruppe II, III, IV. Ihr Aufbau ist ganz analog der Gruppe *Sc* bis *N*. Aber die optische Analyse zeigt kleine Unterschiede. In Gruppe I ist die Struktur des äusseren Niveaus

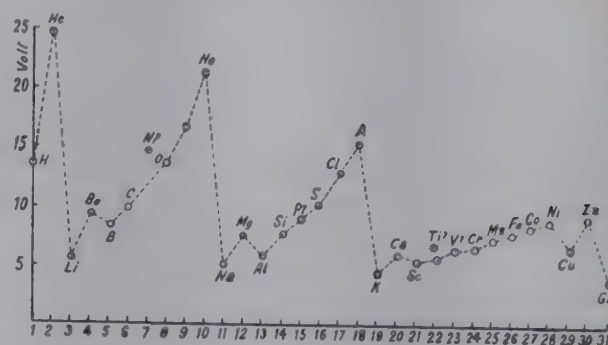


Fig. 4. Ionisierungsspannungs-Kurve.

$$\begin{matrix} xM_2N_1\} \\ (x-1) M_32N_1\} \end{matrix}$$

In Gruppe II ist es bei einigen Elementen

$$\begin{matrix} (x+1)M_3\} \\ xM_3. N_1\} \end{matrix}$$

Vergleicht man z. B. *Ni* und *Pd*

$$\begin{matrix} Ni & \dots & 8M_32N_1\} & Pd & \dots & 9N_3O_1\} \\ Ni & \dots & 9M_3N_1\} & Pd & \dots & 10N_3\} \end{matrix}$$

Ag^+ ist palladiumähnlich, der tiefstliegende Term rührt von $10 N_3$ her, daher überschreitet für *Ag* der normale $10 N_3O_1$ in seinem Energiewert das $9N_32O_1$, wenn es existiert, bedeutend. Daher ist *Ag* gegen *Cu* immer einwertig.

Auch für die seltenen Erden und die Übergangsgruppe III kann man Strukturen angeben; aber die Untersuchung ihrer optischen Spektren ist nur teilweise durchgeführt, und deshalb sind die Strukturen hier nicht gegeben.

Allahabad (Indien), 7. April 1927.

(Eingegangen 28. April 1927).

38. ON THE DETAILED EXPLANATION OF SPECTRA OF THE METALS OF THE SECOND GROUP*

(*Phil. Mag.*, *Sr. VII*, 3, 1265, 1927)

The explanation of the spectra of elements is now making very rapid strides, thanks to the work on the arrangement of electrons inside the atom on the one hand, and development of the principles of non-mechanical vector addition of quantum numbers on the other hand, which we owe to Landé, Russell, Pauli, Heisenberg, Hund¹, and others. The latter authors have so far confined their attention to the fundamental levels of the atom, though in some papers the higher levels have been accounted for on similar lines. In the present paper, an attempt has been made to show that these principles can be extended for finding out all

the higher terms, and in the case of metals of the second group all details of their spectra are explained in a very satisfactory way. The following is a brief sketch of the method of working:—In accordance with Pauli's Principle, we assign to each electron the characteristics of a doublet spectrum. Applied to alkalis, the explanation of the spectrum is very easy. The vibrating electron always comes after a sublevel has been completely closed, hence the atomic residue contributes nothing towards the resultant spectrum. The electron may be supposed to run through all the higher levels, beginning from X_1 . We thus get 2S , 2P , 2D , ... terms,—i.e. a completely developed doublet spectrum. The higher terms arise when the electrons run through the possible higher levels. In the case of alkaline

* Communicated by the Author.

¹ For a complete bibliography, see a paper by Otto Laporte, *Journ. Opt. Soc. Amer.*, July, 1926.

earths, there are two outermost electrons. In the normal case, both are in some X_1 -level. But when the atom is excited, one may be supposed to be at rest; the other runs through all the higher levels. The spectrum observed is due to the combination of the orbits of these two electrons. The rules for combination of orbits were first given by Pauli and developed by Hund and Heisenberg. For the sake of lucidity, I have attached a complete structure diagram. The rules of addition of quantum numbers are also summarized below. It may be added that I claim no originality in this paper except the method of representation, which I have found to be very convenient.

Principles of Orbit Combination

The principles which have so far been developed may be thus briefly summarized:—

Each spectral term may be denoted by the symbol n^r_{kl} (Landé), where r denotes the multiplicity $r = 1, 2, 3, \dots$ for singlets, doublets, triplets, etc.), k =azimuthal quantum number (1, 2, 3, ... for $s, p, d, f, \dots$), j =inner quantum number which is the vector sum of r and k . But for purposes of addition, we do not use r, k as they occur above, but have to use certain associated numbers. Different authors use different symbols with different values: thus Landé uses R, K, J ; Sommerfeld uses j_s, j_a, j ; and Pauli uses $[i, j, k]$. A comparison between the different systems of

symbols is given in a recent paper by Otto Laporte, who finds that the Sommerfeld system is superior to the other two. In the following we adopt the Sommerfeld systems with a slight change. We shall write

i_r , in place of Sommerfeld's j_s ,

i_k , in place of Sommerfeld's j_a

i_j , to denote the effective inner quantum number.

Thus

$i_r = 0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ for singlets, doublets, triplets, etc.

$i_k = k-1, 0, 1, 2, 3$, for $s, p, d, f, \dots$

i_j is calculated from the rule:—

i_j =Vector sum of i_k and i_r in the quantum sense—
i.e. it must have all successive whole or half-numbered values lying between $|i_r + i_k|$ and $|i_r - i_k|$.

For purposes of description, Landé's notation n^r_{kl} may be retained.

Table I. contains a full chart of (i_r, i_j, i_k) values for different systems.

The corresponding magnetic quantum number $i_m = \pm i_j, \pm i_j - 1, \pm i_j - 2$, and thus i_m is the vector sum of i_{mr} and i_{mk} , where

$$\begin{aligned} i_{mr} &= \pm i_r, & \pm i_r - 1, \\ i_{mk} &= \pm i_k, & \pm i_k - 1. \end{aligned}$$

TABLE I
Showing values of i_r, i_k, i_j

ODD MULTIPLETS							EVEN MULTIPLETS							
$i_k \backslash i$	0	1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$i_r \backslash i_k$	
$s = 0$	0				Singlet i_r	0	$\frac{1}{2}$						Doublet $i_r = \frac{1}{2}$	$s = 0$
$p = 1$		1					$\frac{1}{2}$	$\frac{3}{2}$						$p = 1$
$d = 2$			2					$\frac{3}{2}$	$\frac{5}{2}$					$d = 2$
$f = 3$				3					$\frac{5}{2}$	$\frac{7}{2}$				$f = 3$
$s = 0$		1			Triplet $i_r = \frac{1}{2}$			$\frac{3}{2}$					Quartet $i_r = \frac{3}{2}$	$s = 0$
$p = 1$	0	1	2				$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$					$p = 1$
$d = 2$		1	2	3			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$				$d = 2$
$f = 3$			2	3	4			$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$			$f = 3$
$s = 0$			2		Quintet $i_r = \frac{1}{2}$				$\frac{5}{2}$				Sextet $i_r = \frac{5}{2}$	$s = 0$
$p = 1$		1	2	3				$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$				$p = 1$
$d = 2$	0	1	2	3	4		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$			$d = 2$
$f = 3$		1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$		$f = 3$

The change in energy level in weak fields is given by

$$\frac{E}{Oh} = (i_{mr} + i_{mk})g,$$

where

g = Landé's splitting-up factor,

$$O = \text{Larmor's precession factor} = \frac{eH}{4\pi cm}.$$

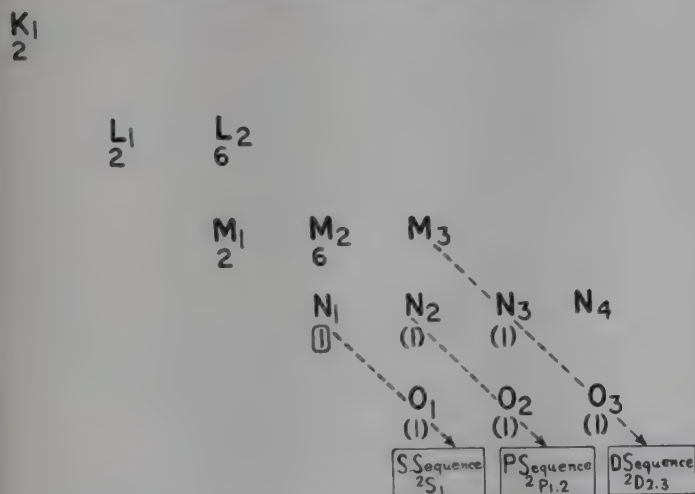
The change in strong fields is given by

$$\frac{E}{Oh} = 2i_{mr} + i_{mk}.$$

We shall have no occasion to use the strong field or weak field magnetic quantum numbers².

The doublet spectrum is supposed to be the fundamental spectrum from which all other complicated spectra can be synthesized. When the constitution is such that there is only one electron left after a sublevel is closed, this electron as it runs through the following levels gives rise to the corresponding doublet terms. Thus we have for Potassium:

STRUCTURE DIAGRAM OF POTASSIUM (19)



ORIGIN OF NORMAL TERMS IN THE SPECTRUM OF K

Russell and Saunders' symbol has been used throughout (*vide* Ap. Journ. vol. lxi. p. 38). (1) denotes the running electron.

Thus the alkali spectrum is most simply explained on the assumption that it is due to the movement of the running electron in the successive higher levels.

[RULES OF SYNTHESIS.]

Alkaline Earths.

In the case of the next group of elements, viz. the alkalis, a second electron is added. If we take Mg, we have the constitution:—

$$\text{Mg} = \left(\begin{array}{cccc} \text{K} & \text{L} & \text{M}_1 & \text{M}_2 \dots \\ 2 & 8 & 1, (1) \rightarrow (1) & \end{array} \right)$$

The optical spectrum is due to the two outer electrons shown under M_1 . In most cases, one electron remains fixed at M_1 , the other runs through the successive levels. The level observed is the vector sum of the levels of these two electrons. As mentioned above, these rules have been developed by Russell, Pauli, Heisenberg, and Hund. Let N_{KJ}^n denote the resultant levels, and let I stand for the Sommerfeld quantum numbers. Then to get a complete knowledge of N_{KJ}^n , we must have a knowledge of the corresponding values of I_K , I_J , I_n . We have

$$I_n = \text{vector sum of } (i_r)_1 \text{ and } (i_r)_2;$$

$$I_K = \text{vector sum of } (i_k)_1 \text{ and } (i_k)_2.$$

The determination of I_J presents the most formidable difficulties. It cannot be defined as the vector sum of $(i_j)_1$ and $(i_j)_2$. We have to write out all the possible magnetic levels for each of the components (1) and (2) and then add them, taking one from each group. Thus:—

The magnetic levels of electron (1) are

$$(i_m)_2 = \pm(i_1)_1, \pm(i_1)_1 - 1, \pm(i_1)_1 - 2, \dots$$

The magnetic levels of electron (2) are

$$(i_m)_2 = \pm(i_2)_2, \pm(i_2)_2 - 1, \pm(i_2)_2 - 2 \dots$$

Thus the above procedure, without any further restriction, would give us

$$\{2(i_j)_1 + 1\} \{2(i_j)_2 + 1\} \text{ values of } I_m.$$

After arranging these values symmetrically, we have to obtain the values of I_J . This will completely define the resultant term I_J .

Applying this rule to Mg, when we have both electrons in the M_1 orbit,

	i_r	i_k	i_j	i_m
for electron (1):	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$ — $\frac{1}{2}$
„ „ (2):	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$ — $\frac{1}{2}$
Resultant:	0 $\frac{2}{2}$	0	0	1 0 1
	I_n	I_K	$I_J = 0$	$I_J = 1$

The resultant orbit has therefore $I_n = 0$ and $\frac{2}{2}$, i.e. it belongs to a singlet or triplet system. $I_K = 0$, i.e. $K = 1$. It is an s-orbit $I_J = 0, 1$. It has the inner quantum number = 0 or 1.

Since 3S_1 is not observed, Pauli lays down a principle which excludes it, viz.: no two electrons in a closed orbit can have identical values of i_m .

This rule excludes 3S_1 , for it arises from $(i_m)_1 = \frac{1}{2}$, $(i_m)_2 = \frac{1}{2}$, or both = $-\frac{1}{2}$.

From this principle also follows Stoner's rule: The number of electrons in a closed group = $2[j \text{ used in Landé's sense}]$. For the resultant magnetic moment due to the component electrons = 0, and this can take place if we assign to each the different possible value of $(i)_m$ for a subgroup. The number = $2j$ or $(2j+1)$, and to every

²The preliminary introduction is taken from Laporte's article in the Journ. Opt. Soc. America, July 1926.

positive value there is a corresponding negative value. Hence the resultant = 0, when there are $2j$ electrons, and each is contained in a different magnetic level. But I do not think that Stoner's subdivision of each higher level L_2 or M_2 into $L_{21} L_{22} M_{21} M_{22}$ is quite justified. See a paper by Saha and Ray in the *Physikalische Zeitschrift*.

Origin of Higher Terms.

But Pauli's principle cannot be applied where the electrons are in different levels. Thus let electron (1) be in the M_1 -orbit, electron (2) in the N_1 -orbit. Here Pauli's rule will not hold; we shall get 2^1S_0 , 2^3S_1 -terms. Similarly, as the electron (2) runs through the higher X_{11} levels it gives rise to the higher members of the 1^1S_0 and 3^1S_1 series, viz. 2^1S_0 , 2^3S_1 , etc.

Combination of M_1 and M_2 Levels.

We have

	i_r	i_k	i_f	i_m	
for electron (1):	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
„ „ (2):	$\frac{1}{2}$	1	$(\frac{1}{2}, \frac{3}{2})$	$(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{3}{2})$	$(\frac{1}{2}, -\frac{1}{2})$
0	$\frac{3}{2}$	1	0		$I_f=0$
I_r	I_k		1 0 1		$I_f=1$
			2 1 0 1 2		$I_f=2$
			1 0 1		$I_f=1$

The resultant orbit will be 1^1P_1 , $3^1P_{0,1,2}$. The number of magnetic levels for these terms is $3 + (1 + 3 + 5) = 12$. The possible numbers of combinations of $(i_m)_1$ and $(i_m)_2$ are 2 and 6, and if we write them out, and add for the resultant I_m , and write out the corresponding values of J , we get the P terms ($2^1S_{\frac{1}{2}}$, $2^1P_{\frac{1}{2}}$) give us 1^1P_1 , 3^1P_0 , and ($2^3S_{\frac{1}{2}}$, $2^3P_{\frac{3}{2}}$) give us 3^1P_1 , 3^1P_2 .

Combination of N_1 and N_3 Levels.³

We need not repeat the summation for i_r . Now $I_k=2$, or the resultant are D-terms, 1^1D_2 , $3^1D_{1,2,3}$. The values of i_f are $\frac{1}{2}$ and $(\frac{5}{2}, \frac{3}{2})$ respectively. $(\frac{1}{2})$, $(\frac{3}{2})$ give us 1^1D_2 , 3^1D_1 , and $(\frac{1}{2})$, $(\frac{5}{2})$ give us $3^1D_{2,3}$. In this way we get by combination with levels N_2 the higher Rydberg terms of 1^1P_1 and $3^1P_{0,1,2}$. Combination with N_4 gives us the first F-terms.

We thus get a general explanation of the regular term-sequences in the spectrum of Mg, and *mutatis mutandis* for Ca, Sr, and Ba as well. But the procedure is capable of yielding still further results. It is known to spectroscopists that, in spite of the similarity amongst the spectra of these elements, there are certain outstanding differences. For the spectrum of Mg, the highest value for the sequence $D=15268.7$, while the highest D-values for Ca, Sr, and

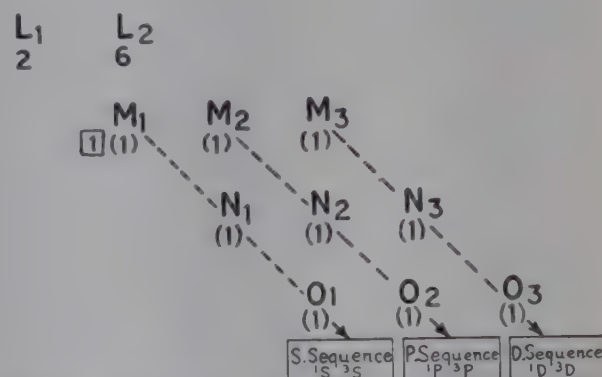
Ba are much higher; in fact they sometimes exceed the P-values, as the following table shows:—

	D.	P.
Mg	1^1D_2 15268.7	1^1P_1 26620.7
	3^1D_2 13714.7	3^1P_1 39801.4
Ca	1^1D_2 27455.3	1^1P_1 25652.4
	3^1D_2 28955.2	3^1P_1 34094.6
Sr	1^1D_2 25786.8	1^1P_1 24238.1
	3^1D_2 27717.7	3^1P_1 31432.2
Ba	1^1D_2 30634.1	1^1P_1 23969.2
	3^1D_2 32814.1	3^1P_1 29392.8

These large D-values can be easily explained if we compare the Structure Diagrams of Mg and Ca.

STRUCTURE DIAGRAM OF Mg (12)

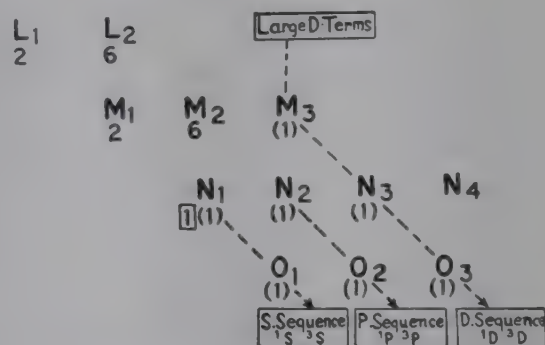
K_1
2



ORIGIN OF NORMAL TERMS IN MAGNESIUM

STRUCTURE DIAGRAM OF CALCIUM (20)

K_1
2



ORIGIN OF NORMAL TERMS IN THE SPECTRUM OF Ca

A comparison of the two structure diagrams shows that the successive positions of the running electron in Mg are M_1 (1^1S_0), M_2 (1^1P and 3^1P), M_3 (1^1D and 3^1D), and we have approximately $1^1P = \frac{N}{2^2}$, $1^1D = \frac{N}{3^2}$. But in Ca the positions

³Fowler, Report on Series in Line Spectra, ch. xiv.

K ₁ 2					Transitional group I.	Transitional group II.	Rare earths I.	Transitional group III.
1 H 2 He	2K ₁				21 Sc M ₂ 2N ₁ 2M ₁ N ₁ 22 Ti 2M ₁ 2N ₁ 3M ₁ N ₁ 23 V 3M ₁ 2N ₁ 4M ₁ N ₁ 24 Cr 5M ₁ 2N ₁ 4M ₁ 2N ₁ 25 Mn 5M ₁ 2N ₁ 6M ₁ N ₁ 26 Fe 6M ₁ 2N ₁ 7M ₁ N ₁ 27 Co 7M ₁ 2N ₁ 8M ₁ N ₁ 28 Ni 8M ₁ 2N ₁ 9M ₁ N ₁	39 Y 2N ₁ O ₁ N ₁ 2O ₁ 40 Zr 3N ₁ O ₁ 2N ₁ 2O ₁ 41 Nb 4N ₁ O ₁ 3N ₁ 2O ₁ 42 Mo 5N ₁ O ₁ 4N ₁ 2O ₁ 43 Ma 6N ₁ O ₁ 5N ₁ 2O ₁ 44 Ru 7N ₁ O ₁ 6N ₁ 2O ₁ 45 Rh 8M ₁ O ₁ 7M ₁ 2O ₁ 46 Pd 10N ₁ 9N ₁ O ₁	57 La 58 Ce 59 Pr 60 Nd 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tu 70 Yb	71 Lu 72 Hf 2O ₁ 2P ₁ 3O ₁ P ₁ 73 Ta 3O ₁ 2P ₁ 4O ₁ P ₁ 74 W 4O ₁ 2P ₁ 5O ₁ P ₁ 75 Re 5O ₁ 2P ₁ 6O ₁ P ₁ 76 Os 6O ₁ 2P ₁ 7O ₁ P ₁ 77 Ir 7 O ₁ 2P ₁ 8 O ₁ P ₁ 78 Pt 9O ₁ 2P ₁ 9O ₁ P ₁
3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne	2K ₁ 2L ₁ 2L ₁ 2L ₁ 3L ₁ 4L ₁ 5L ₁ 6L ₁	L ₁ L ₂						
11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 A	6L ₁ 6L ₁ 2M ₁ 2M ₁ 3M ₁ 4M ₁ 5M ₁ 6M ₁	M ₁ 2M ₁ M ₁ 2M ₁ 3M ₁ 4M ₁ 5M ₁ 6M ₁	M ₁ 2	M ₂ 6	M ₃ 10			
29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr	10M ₁ N ₁ 9M ₁ 2N ₁ 10M ₁ 2N ₁ 2N ₁ N ₁ 2N ₁ 2N ₁ 3N ₁ 4N ₁ 5N ₁ 6N ₁			N ₁ 2	N ₂ 6	N ₃ 10	N ₄ 14	
47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe	10N ₁ O ₁ 2O ₁ 2O ₁ 2O ₁ 3O ₁ 4O ₁ 5O ₁ 6O ₁				O ₁ 2	O ₂ 6	O ₃ 10	
79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 Rad Tc 86 Nt	10O ₁ 2P ₁ 2P ₁ P ₁ 2P ₁ 3P ₁ 4P ₁ 5P ₁ 6P ₁					P ₁ 2	P ₂ 6	P ₃ 10
							Q ₁ 2	Q ₂ 6

(Explanation of the Chart.)

[The chart is a modification of the earlier schemes of Bohr and Stoner. The L₂₁ and L₂₂ levels of Stoner are compounded into one L₂-level. (For explanation, see a paper by Saha and Ray in the *Physikalische Zeitschrift*.) The chart explains the formation of (1) the regular groups, (2) the transitional groups, (3) the rare earths, and gives the electronic composition of the outer shells of the electrons, as obtained from Hund's interpretation of complex spectra (*Zs. j. Phys.*, vols. xxxiii & xxxiv.). The same chart explains

the periodic classification, and the spectra of elements. The distinctive nature of the small groups of two, consisting of an alkali and alkaline earth, is clearly brought out. They are formed when any X₁-level (X=K, L, M, N...) is filled, just as the regular groups are obtained when X₂ is filled, transitional groups when X₃ is being filled, as rare earths when X₄ (X=N) is being filled.

For the explanation of spectra with the same chart, see the text.]

are N_1 (1S_0), N_2 (1P , 3P), and then M_3 not N_3 , which is on a higher level. Now the 1D -term corresponding to N_3 has the normal value, i.e. $Ca \frac{N}{3^2}$, but the 1D -term corresponding to M_3 must have a higher value, i.e. $Ca \frac{N}{2^2}$. This diagram, therefore, symbolically explains the origin of the large D-terms in Ca and also in Sr and Ba. In the spark spectrum of Ca^+ , it explains why the first of 2D -terms is larger than 2P , while in the spectrum of Mg^+ , 2P is $> ^2D$.

Concluding Remarks.

The foregoing work shows that the above scheme of electron arrangement, which is a modification of Stoner's scheme, combined with the rules of synthesis of complicated spectra from the elementary component doublet spectra, gives a very satisfactory explanation of the fundamental as well as of all the higher terms regular and anomalous, of the alkaline earths. Even the detailed differences (e.g. occurrence of large D-terms in Ca, Ba, Cr, and its absence in Mg) are readily explained. But the theory goes still further. It gives us a clue to the origin of dashed terms. They arise when the stationary electron is in the metastable orbit, and the running electron is in the same orbit or in the higher homologous orbit. We can also obtain some clue

regarding the term values. If the orbit arises when both electrons are in the same shell, or the running electron in the previous unclosed shell, the values are large. No matter whether we get S, P, D, F, or G terms, the order of the value will be the same, when the origin of these terms is common. The origin of dashed terms is taken in a subsequent paper.

Thus note that when both electrons in Ca are in M_3 -levels, we get 3F , 3P , 1G , 1D , 1S_0 terms. Their order of value is the same.

But if the running electron is in a higher shell, it will give rise to higher Rydberg terms; the values will decrease

approximately as $\frac{N}{m^2}$, $m=1, 2, 3$ respectively.

The investigation also shows that differences are expected between the spectra of Ca and Ba. These points are being investigated. It is also apparent that for the calculation of the higher Rydberg terms Pauli's rule is not necessary, and we no longer need the complex calculation involving the magnetic quantum numbers.

In conclusion, the author wishes to express his thanks to Mr. K. Mazumder, who has drawn the charts and tables for him.

39. ON THE EXPLANATION OF SPECTRA OF METALS OF GROUP II*

(PART II)

P. K. KICHLU AND M. N. SAHA

(*Phil. Mag., Sr. VII*, 4, 193, 1927)

In a previous paper one of us¹ has discussed the origin of the higher Rydberg sequence terms in the normal spectra of elements of group II. It is well known that besides these normal terms all these elements give a number of anomalous terms. They were noticed by Rydberg² in 1894 in the spectra of Ca and Sr, and Popow³ discovered similar groups in the spectra of Ba and Al in 1915. In 1921, Götze⁴ interpreted these groups as a transition between the normal p -group and another group which he called p' (sometimes also called $\bar{p}$, which notation we shall follow. That the $\bar{p}$ -group was essentially of the same nature as the ordinary p was made clear from investigation of the Zeeman effect of these groups.

Since this time numerous groups of dashed (or barred) terms have been discovered in the spectra of elements of higher groups; but the first indication of the origin of these terms was given by Russell and Saunders⁵, and independently by Wentzel.⁶ Russell and Saunders discovered other groups of $p\bar{p}$ and $d\bar{d}$ combinations in spectra of Ca, Sr, and Ba. These $\bar{p}$ and $\bar{d}$ terms are sometimes negative, and the abovementioned authors noted that if a certain number was added to these terms they formed approximately a Rydberg sequence. This number was approximately 13700 in the case of Ca, which is about the same as the difference between the values of the fundamental 2S -term of Ca^+ and the next term in order of value, viz. 2D . From this fact the above-mentioned authors concluded that the anomalous

*Communicated by the Authors.

¹M. N. Saha, *Phil. Mag.*, June 1927.

²Rydberg, *Wied. Ann.* lii. p. 119 (1891).

³Popow, *Ann. der Physik*, Bd. xlv. p. 147 (1914).

⁴Götze, *Ann. der Physik*, Bd. lxxvi. p. 285 (1921).

⁵Russell and Saunders, *Astrophysical Journal*, lxi. p. 38 (1925).

⁶Wentzel, *Phys. Zeits.* xxiv. p. 106 (1923); xxv. p. 182 (1924).

terms arise when the stationary electron of Ca is in the metastable M_3 -level.

In this investigation it will be shown that the conclusion of these authors regarding the origin of $\bar{p}$ -terms is correct in the case of Ca, Sr, and Ba; but from this it is not safe to draw any general conclusion regarding the nature of the dashed terms. As was pointed out in the note on the spectrum of Neon⁷ by the senior author, whenever from any particular distribution of electrons in potential orbits F, D, P terms simultaneously arise, they must then have the same combinatory powers, so that if F and P are treated like ordinary terms, D must be dashed. But we can also dash F and P and treat D as an undashed term. It is purely a matter of convention, in which we have to be guided by our previous knowledge of the history of the spectrum of the element.

Origin of $P\bar{P}$ -Terms in the Spectrum of Mg, Zn, Cd, etc.

As Bowen⁸ and Millikan have pointed out, $P\bar{P}$ -terms are known in the spectra of Mg, Zn, and Cd, for which the metastable level of the ionized element is not 3D , but 2P . Bowen and Millikan, by their hot-spark method, were able, to discover $P\bar{P}$ groups in the spectra of Be, B^+ , C^{++} , N^{+++} , O^{++++} , and in Al^+ , Si^{++} , P^{+++} , S^{++++} , Cl^{+++++} , which have got a structure similar to that of Mg. They discovered the most interesting laws regarding the values of these $P\bar{P}$ -groups, and showed theoretically as well as experimentally that the values of these $P\bar{P}$ -groups were approximately the same as the value of the fundamental line ($^1S-^1P$) of these elements. Sawyer and Bees, in a note to 'Nature' of Dec. 26, 1925, however, find that in the case of Zn and Cd the values of $P\bar{P}$ -groups are the mean between the values of ($^1S-^1P$) of the normal element and $^2S-^2P$ of the ionized element. We shall not dwell upon Bowen and Millikan's explanation of the origin of these terms at this place, as this will come out later on in the course of discussion.

All these facts, and the other details discovered by Russell and Saunders in the spectra of Ca, Sr, and Ba, receive a unitary explanation on the lines suggested in the former paper of the senior author⁹ and in the note on the spectrum of Neon. We shall begin by writing down the structure diagram for Mg and Ca.

Structure Diagram for Mg (12)

K_1							
2							
	L_1	L_2					
	2	6					
		M_1	M_2	M_3			
		2					
			N_1	N_2	N_3	N_4	
				O_1	O_2	O_3	

Structure Diagram for Ca (20)

K_1							
2							
	L_1	L_2					
	2	6					
		M_1	M_2	M_3			
		2	6				
			N_1	N_2	N_3	N_4	
			2				

The normal state of Mg is obtained by keeping both the electrons in M_1 ; in the case of Ca, both in N_1 . For transitions to higher levels, one electron has to be kept at M_1 for Mg, and at N_1 for Ca: the other electron has to be successively shifted to all positions on the right. Terms arising from levels on the same vertical column will have approximately the same scale of values, while they will decrease progressively as we pass to further columns on the right. It is emphasized at this point that we assign the total quantum number 1 to those terms which have their origin in the undisturbed outermost level. Thus the term arising from the combination $M_1 M_1$, viz. 1S_0 , has the total quantum number 1. As the electron is shifted to successive levels on the right, the total quantum number increases by one at each step. This method of fixing up the total quantum number for optical terms is evidently more appropriate for expressing actual facts than Bohr's representation of terms by $3S$ (for Mg, M_{11}), $4S$ (for Ca, same as N_{11}), etc., though the latter method of representation has the merit of giving a unitary representation to the X-ray levels as well as optical levels.

The normal terms of Mg are therefore due to combinations:

(a) $M_1 M_1$ (both the electrons in M_1) giving 1S_0 only as first pointed out by Pauli¹⁰.

$M_1 N_1$, $M_1 O_1$, $M_1 P_1$, ... will give higher Rydberg sequences of 1S_0 -term, and a sequence of 3S_1 -terms beginning with 2^3S_1 (form $M_1 N_1$ in the case of Mg).

(b) $M_1 M_2$ (one electron is in M_1 , the running electron is in M_2).

Terms obtained: 1P , 3P .

$M_1 N_1$, $M_1 O_2$, $M_1 P_2$, ... give higher Rydberg sequence terms to this set of singlet and triplet P's. The P-sequence begins with the total quantum number 2.

(c) $M_1 M_3$ (the running electron is M_3).

Terms obtained: 1D , 3D .

$M_1 N_3$, $M_1 O_3$, $M_1 P_3$, ... give the Rydberg sequence. The D-sequence will begin with the total quantum number 3.

In the case of Ca,

(a) $N_1 N_1$... give us 1S_0 , and

$N_1 O_1$, $N_1 P_1$, ... give us the 1S and 3S series.

(b) $N_1 N_2$ give us the first 1P and 3P terms and

$N_1 O_2$, $N_1 P_2$ the higher 1P and 3P Rydberg terms.

⁷M. Saha, Phil. Mag.

⁸Millikan and Bowen, Phys. Rev. xxv. p. 150 (1925).

⁹M. N. Saha, Phil. Mag., June 1927 and "Note on the Spectrum of Neon" (Phil. Mag., July 1927, p. 223).

¹⁰W. Pauli, Jun., Zs. für Physik, Bd. xxxi. p. 765 (1925).

In the (c) combination the first combination is $N_1 M_3$, and not $N_1 N_3$. As the M_3 -level has at least the same order of value as N_3 , $N_1 M_3$ will give us 1D and 3D terms of the same order of value as the first 1P and 3P terms. This explains the occurrence of large D-terms in the spectrum of Ca, and *mutatis mutandis* in Sr and Ba. Thus in Ca, Sr, and Ba the D-sequence will begin with 2, and not with 3 as in Mg.

If we write out the structure diagrams for Zn and Cd, we see that the normal spectrum will be exactly like that of Mg. No D-terms comparable in value to the first P-terms will occur, and the sequence will begin with the total quantum number $n=3$.

Structure Diagram for Zn (30)

K_1 2						
	L_1 2	L_2 6				
		M_1 2	M_2 6	M_3 10		
			N_1 2	N_2	N_3	N_4

(Both electrons are in N_1 . The next transition is horizontally from N_1 to N_2 . M_3 is completely filled). A number of anomalous terms is possible from the combination $9M_3, 2N_1N_2$, giving $^3F, ^3D, ^3P, ^1F, ^1D, ^1P$, but it is not yet known whether they exist.

Structure Diagram for Cd (48)

K_1 2						
	L_1 2	L_2 6				
		M_1 2	M_2 6	M_3 10		
			N_1 2	N_2 6	N_3 10	N_4
				O_1 2	O_2	O_3

(In normal case other electrons are in O_1 . Transition is horizontally from O_1 to O_2 , giving O_1O_2 as the next state. N_3 is completely filled up. Here also the $9N_3, 2O_1O_2$ combination is possible).

In order to account for the anomalous terms, let us put one electron permanently in the next higher level and move the second electron through the next successive levels. In the case of Mg, Zn, and Cd there is no metastable level diagonally across the fundamental level. Thus, taking the case of Mg, the level M_1 will be kept entirely empty: one electron will be kept permanently at M_2 , the second electron will be moved successively through the $M_2, M_3, N_1, N_2, N_3, \dots$ levels. In Ca, however, the level next to the fundamental is M_3 , so that the fixed electron will be always at M_3 , and the running electron will move through the other possible levels, viz. $N_1, M_3, N_2, \dots$. For this reason the large D-terms

which arise from the combination $M_3 N_1$ may be considered as the first of the anomalous terms in Ca.

Anomalous Terms in Mg, Zn, Cd.

Let us now find out, by applying the combination rules of Pauli, Heisenberg, and Hund, the probable anomalous terms in the spectra of Mg, Zn, and Cd.

(a) $M_2 M_2$ give $^3P_{0,1,2}, ^1D_2, ^1S_0$.

The P's will be dashed, because $M_1 M_2$ give us $^3P_{0,1,2}$, and transition is possible between $(M_1 M_2)$ and $(M_2 M_2)$.

Value of $^3P_{0,1,2}$.

Let us consider the relative values of the following sequences for Mg:—

$M_1 M_2$ 1^3P	$M_1 N_2$ 2^3P	$M_1 O_2$ 3^3P	$M_1 P_2$ 4^3P	$M_1 Q_2$ 5^3P
$M_2 M_2$ 1^3P	$M_2 N_2$ 2^3P	$M_2 O_2$ 3^3P	$M_2 P_2$ 4^3P	$M_2 Q_2$ 5^3P

Taking corresponding pairs of higher Rydberg terms, say 5^3P and $5^3\bar{P}$, we find that the second electron is in both cases far out. The atomic residue will therefore exert, on the inner of the two valence electrons, approximately the same force in both cases. In other words, we can write symbolically

$$(5^3P \rightarrow 5^3\bar{P}) = (M_1 Q_2) \rightarrow (M_2 Q_2) \\ = (M_1 \rightarrow M_2) Q_2$$

The symbol in the last step denotes that the energy of the electron in the Q_2 position has the same value in both cases because it is far out, hence $5^3P - 5^3\bar{P} = (M_1 \rightarrow M_2)$ of the atomic residue. This atomic residue is, however, the Mg^+ electron, M_1 corresponds to the fundamental 2S of Mg^+ , and M_2 corresponds to the 3P of Mg^+ . We therefore arrive at the rule that for the higher terms

$$(^3P - ^3\bar{P}) \text{ of } Mg = (^2S - ^2P) \text{ of } Mg^+.$$

When we pass on, however, to the lower terms like $2^3P - 2^3\bar{P}$, the influence of the atomic residue on the running electron can no longer be regarded as the same in both cases. Hence the above rule will not hold so well.

Taking

$$1^3P - 1^3\bar{P} = (M_1 M_2 - M_2 M_2),$$

we find that the transition is obtained by moving one electron from M_1 to M_2 , the other electron always remaining at M_2 , i.e.,

$$\begin{array}{ccc} M_1 & & M_2 \\ 1 & & 1 \dots ^3P. \\ \rightarrow & & 1, 1 \dots ^3\bar{P}. \end{array}$$

The difference in energy may be assumed to be approximately the same as is required in the passage of the electron from $M_1 \rightarrow M_2$ from the $M_1 M_1$ -stage:

$$\begin{array}{ccc} M_1 & & M_2 \\ 1, 1 & & \dots ^1S_0 \\ \rightarrow & & 1 \dots ^3P, ^1P, \end{array}$$

the difference being that in the first case the transition is

with the stationary electron at M_2 , in the second case it is with the stationary electron at M_1 . Hence

$$\begin{aligned} {}^1\text{S}-{}^1\text{P} \text{ is } &> {}^1\text{S}-{}^1\text{P} \text{ of the metal} && \dots (\text{A}) \\ \text{and} &< {}^2\text{S}-{}^2\text{P} \text{ of the ionized metal} && \dots (\text{B}) \end{aligned}$$

Rule (A) is given (with=instead of $>$) by Bowen and Millikan¹¹, whose arguments are almost the same as that given here: rule (B) is given by Sawyer and Beese, who make ${}^3\text{P}-{}^3\text{P}$ equal to the mean value of

$$({}^1\text{S}-{}^1\text{P}) \text{ of } M \text{ and } ({}^2\text{S}-{}^2\text{P}) \text{ of } M^+$$

for Zn and Cd. The validity of the above rules will be apparent from the following table:—

TABLE I.

Element	Value of P—P.	${}^1\text{S}-{}^1\text{P}$ of M.	${}^2\text{S}-{}^2\text{P}$ of M^+
Mg	35982	35051	35669
Zn	47894	46745	48482
Cd	44088	43692	44135
Hg	?	54099	?
Al ⁺	56690	59845	53918
Si ⁺⁺	76986	82878	71280
P ⁺⁺⁺	97037	105190	88649
S ⁺⁺⁺⁺	116985	127144	105866
Cl ⁺⁺⁺⁺⁺	136928	148949	123001

The figures in Table I, as well as theoretical arguments, show that Sawyer and Beese's rule represents facts more accurately than Millikan and Bowen's rule. The ${}^1\text{D}_2$, and ${}^1\text{S}_0$ -terms expected from M_2M_2 -combination has also been recently obtained by one of us in Mg.

Higher negative terms may be obtained by keeping the first electron at M_2 , and allowing the other electron to run through the higher levels M_3 . . . Though they are not yet known, one typical example may be given:—

Combination $M_2 M_3$ will give us

$$\begin{array}{ccc} {}^3\text{F} & {}^3\text{D} & {}^3\text{P} \\ {}^1\text{F} & {}^1\text{D} & {}^1\text{P} \end{array}$$

${}^3\text{F}$ will have the highest (*i.e.* lowest negative) value. They may be expected to have the value ${}^1\text{D}$ of Mg —35000, *i.e.* about —20000 for Mg. If they exist, they will combine with the ${}^1\text{D}$, ${}^3\text{D}$ terms of Mg.

Origin of Anomalous Terms in Ca, Sr, and Ba.

Bowen and Millikan have pointed out that PF -multiplets of the above description have not yet been discovered in the spectra of Ca, Sr, and Ba. The fact receives a clear explanation when we look at the structure diagrams of these elements.

Structure Diagram for Sr (38)

2K				
8L				
18M				
	N_1	N_2	N_3	N_4
	2	6		
		O_1	O_2	O_3
		2		

(Normal terms are obtained by keeping one electron permanently at O_1 and allowing the other to run through O_1 , O_2 , N_3 . . .; for anomalous terms, keep the electron at N_3 and let the other run through the levels O_1 , N_2 , O_3 , etc.)

Structure Diagram for Ba (56)

2K				
8L				
18M				
	N_1	N_2	N_3	N_4
	2	6	10	
		O_1	O_2	O_3
		2	6	
			P_1	P_2
			2	

(To get the normal terms, one of the two electrons is placed at P_1 and the other moves through P_1 , N_4 , O_3 , P_2 . . . The N_1P_4 combination, which is expected to give a large ${}^1\text{F}$ and ${}^3\text{F}$ term, is not yet known with certainty.)

For Ca M_3 is the level next in value to N_1 , and we keep the first electron in this level. The anomalous terms are then obtained by allowing the other electron to run through the other possible levels. We get the following combinations:

(a) M_3M_3

Since both electrons are in M_3 -orbit (Pauli's rule will apply), we obtain:

$${}^3\text{F}, {}^3\text{P}, {}^1\text{G}_4, {}^1\text{D}_2, {}^1\text{S}_0.$$

State ($N_1 M_3$) giving ${}^3\text{D}$, ${}^1\text{D}$ will not combine with $M_3 M_3$, because $N_1 \rightarrow M_3$ is forbidden. Hence the D-terms arising from this combination will be of the same nature as the D-terms from M_3M_3 , *i.e.* they are not dashed. This enables us to fix the nature of the other terms. M_3N_3 , M_3O_3 . . . will give us the higher members of the group:

$$\begin{array}{|c|c|c|c|c|} \hline {}^3\text{G} & {}^3\text{F} & {}^3\text{D} & {}^3\text{P} & {}^3\text{S} \\ {}^1\text{G} & {}^1\text{F} & {}^1\text{D} & {}^1\text{P} & {}^1\text{S} \\ \hline \end{array}$$

(b) M_3N_2

This combination gives us

$$\begin{array}{ccc} {}^2\text{F} & {}^2\text{D} & {}^2\text{P} \\ {}^2\text{F} & {}^2\text{D} & {}^2\text{P} \end{array}$$

M_3O_2 , M_3P_2 . . . gives the higher members of the sequence.

(c) M_3O_1

This combination gives us

$${}^3\text{D}, {}^3\text{D}$$

These terms will form higher Rydberg sequence of displaced type with the large ${}^3\text{D}$ and ${}^1\text{D}$. Evidence of their

¹¹Bowen and Millikan, Phys. Rev. vol. xxv. p. 150 (1925).

existence has been obtained in the spectrum of Ba. For reasons stated before

$$\begin{aligned} {}^1\text{D of Ca} &= {}^1\text{P of Ca} + ({}^1\text{S}-{}^3\text{D}) \text{ of Ca} & \dots (A) \\ \text{or} & + ({}^1\text{S}-{}^1\text{D}) \text{ of Ca} & \dots (B) \end{aligned}$$

Relation (A) will be approximately correct, but (B) indicates only an upper limit. The same argument will hold for Sr and Ba. The values of ${}^2\text{S}_1-{}^2\text{D}_3$ for Ca^+ , Sr^+ and Ba^+ , and ${}^1\text{S}_1-{}^3\text{D}_2$ and ${}^1\text{S}_1-{}^1\text{D}_2$ for Ca, Sr and Ba are shown below:—

TABLE II.

	M		M ⁺
	(¹ S- ³ D ₂).	(¹ S- ¹ D ₂).	² S ₁ - ² D ₃ .
Ca	20350	21850	13650
Sr	18219	20149	14557
Ba	9215	11395	4884

M=neutral element; M⁺=ionized atom of the element.

In Barium we have followed Paschen's¹⁴ identification of the D-term. According to Fowler¹⁵ ${}^2\text{S}-{}^2\text{D}$ for $\text{Ba}^+=11990$.

A preliminary comparison with the new terms obtained by Russell and Saunders shows that the above conclusions are well verified. The detailed identification is shown in Table III.

Table III shows that Russell and Saunders' f'' , p'' , and d' terms can be identified with the ${}^3\text{F}$, ${}^3\text{P}$, and ${}^3\text{D}$ terms arising from the M_3N_2 combination. In fact they observe that f'' and p'' are in all respects like ordinary f and p terms. They also follow the usual rule which has been brought to light by Hund¹⁶ and others, that when from the same combination F, D, and P terms arise, F is usually $> \text{D} > \text{P}$.

A number of singlet terms have been mentioned by Russell and Saunders, but their nature has not yet been clearly elucidated. We have therefore refrained from trying to identify them with singlet terms ${}^1\text{F}_3$, ${}^1\text{D}_2$, ${}^1\text{P}_1$. But in the case of Ca, we can hazard the identification mentioned in Table III. Of these, $\text{Y}={}^1\text{F}_3$ seems to be pretty certain. X may be put= ${}^1\text{D}_2$, but it seems to be very difficult to fix up the nature of the "x". Back¹⁷ finds from Zeeman-effect data that "x" is not a singlet term, but a triplet term, ${}^3\text{F}_2$. He has also given ${}^3\text{F}_3$, ${}^3\text{F}_4$. But he finds that the splitting

TABLE III

State	Present notation	Russell & Saunders' notation	Term values					
			Ca		Sr.		Ba.	
(a) M ₃ M ₃	³ F _{4,3,2}	..					19077.9	432.2
							19510.1	480.2
					19990.3			
	³ P _{2,1,0}	p'	10753.0	86.8	10250.7	247.8	18110.5	438.8
10839.8			47.3	10525.5	206.3	18549.3	271.0	
10887.1				10731.8		18820.3		
¹ S ₀ ¹ D ₂ ¹ G ₄	X	8584.9		8964.9		9929.0		
(b) M ₃ N ₃	³ F _{4,3,2}	f''	13407.6	78.3	12006.0	329.7	18372.6	709.5
			13485.9	88.0	12335.7	322.8	19082.1	882.7
			13573.9		12658.5		19964.8	
	³ D _{3,2,1}	d'	11045.3	40.0	9365.9	177.5	17049.8	448.3
			11085.3	26.7	9543.4	117.8	17498.1	339.5
			11112.0		9661.1		17837.6	
	³ P _{2,1,0}	p''	9964.3	4.8	8588.5	33.7	16073.1	252.4
			9969.1	1.9	8622.2	10.8	16325.5	62.0
			9971.0		8633.0		16387.5	
	¹ F ₃ ¹ D ₂ ¹ P ₁	Y	8767.0		9836.1		15213.4	
(c) M ₃ O ₁	³ D _{3,2,1} ¹ D ₂						13475.2 ¹²	
							4526 ¹³	

¹² Identified by Russell and Saunders, *loc. cit.*

¹³ We have for Ba, ${}^3\text{D}_{3,2}-4526=12523.18$ (1), 12972.3 (8u);
 b ${}^3\text{F}-4526=14556$ (6r).

¹⁴ Paschen and Götze, 'Serienspektren,' Chap. on Barium.

¹⁵ A. Fowler, 'Series in Line-Spectra', p. 137 (1922).

¹⁶ F. Hund, *Zs. für Physik*, Bd. xxxiii. p. 841 (1925).

¹⁷ Back, *Zs. für Physik*, Bd. xxxiii. p. 584.

factor g for Zeeman effect is different ($\frac{3}{4}$) in the case of 3F_2 from the value of g given by Landé's formula ($\frac{2}{3}$), and sees in this a justification of Landé's "Verzweigungs-prinzip." The nature of the large term W , or of Z also, cannot be fixed up from the present data. It may be added that Russell and Saunders have taken only those lines which are given by King from his furnace-spectra data. If the full list of arc lines is taken from Kayser and Konen's '*Handbuch der Spektroskopie*,' vol. vii., it is found that there are many lines yet to be classified.

Values of the Terms.

The identification is rendered more probable from the following theoretical considerations about their values :—

It will be seen that the Barium values of anomalous terms are much larger than Ca or Sr values. Further, the terms arising from M_3N_2 combination have the same order of value as those arising from M_3N_3 combination. Let us consider the sequence of terms arising from the following pairs of combinations :—

M_3N_2 $^1D, ^3D$	M_3O_2 $2^1D, 2^3D$	M_3P_2 $3^1D, 3^3D$	M_3Q_2 $4^1D, 4^3D$	M_3R_2 $5^1D, 5^3D$
N_1N_2 $^1P, ^3P$	N_1O_2 $2^1P, 2^3P$	N_1P_2 $3^1P, 3^3P$	N_1Q_2 $4^1P, 4^3P$	N_1R_2 $5^1P, 5^3P$

Of the set of terms arising from $M_3X_2 \dots$ we have taken only the D's. Compare the values of each corresponding pair in each vertical column.

Now,

$$M_3R_2 \rightarrow N_1R_2 = (M_3 \rightarrow N_1)R_2 \\ = (M_3 - N_1) \text{ of } Ca^+ \text{ approximately} \\ = (^2S - ^3D) \text{ of } Ca^+.$$

$$\therefore 5^3D \text{ of } Ca = 5^3P \text{ of } Ca - (^2S - ^3D) \text{ of } Ca^+ \dots \dots \dots (A)$$

The value of 3D and other terms like $f''(^3F)$ arising from this level will therefore lie between the limits :

	Actual values			
	$^3p_2 - (^1S - ^2D)$	$^3p_2 - (^2S - ^2D)$	f''	3D
For Ca	12139	20338	13485	11085
Sr	10888	16480	12335	9543
Ba	17120	23631	19082	17498

1 3D values are thus seen to be slightly lower than the lower limit, and b 3F values higher than the lower limit. Higher Rydberg terms to the above set have not yet been obtained in sufficient number to enable us to make a satisfactory comparison and to see whether a member like

$$5^3D = 5^3P - (^2S - ^2D) \text{ of } M^+$$

also follows the expected order.

Values of Terms arising from M_3M_2 -levels.

Compare, as before, the set of values arising from the combinations:

M_3M_2 $^1P, ^3P$	M_3N_2 $2^1P, 2^3P$	M_3O_2 $3^1P, 3^3P$	M_3P_2 $4^1P, 4^3P$	M_3Q_2 $5^1P, 5^3P$
N_1M_2 $^1D, ^3D$	N_1N_2 $2^1D, 2^3D$	N_1O_2 $3^1D, 3^3D$	N_1P_2 $4^1D, 4^3D$	N_1Q_2 $5^1D, 5^3D$

By the same argument as before the values of the higher terms like 5^3P will approximately be equal to

$$5^3D - (^2S - ^2D) \text{ of } M^+,$$

while the value of 1 3P will be between 1 $^3D - (^1S - ^1D)$ of M and 1 $^3D - (^2S - ^2D)$ of M^+ . The following table shows the expected values of 4P compared to the limits calculated as above:—

	Limits	3P
Ca	7106-15666	10839
Sr	7567-13159	10525
Ba	21419-27930	18549

The value of 3P in the case of Ca and Sr is approximately the mean of the limits. But the Ba value of 3P is less than even the lower limit.

The above comparison explains a feature of the Barium spectrum. The anomalous terms are much larger than the corresponding terms in Ca and Sr. It is easily seen that it is due to the smaller value of the shift numbers $^1S - ^1D$ and $^2S - ^2D$ in the case of Ba. The value of the terms arising from X_3Y_2 and X_3X_3 -levels are of the same order, since 3P and 3D terms have the same order of value. In Barium 3D is much larger than 3P , and we therefore find that the terms arising from X_3X_3 are much larger than the terms arising from X_2Y_3 .

The Rydberg Sequence of Anomalous Terms.

Rydberg sequence has been established satisfactorily up to the fifth term only in the case of Ca 3P terms. The comparison of values is given below :—

	1^3P	2^3P	3^3P	4^3P	5^3P
	10840	767	-4983	-8313	-10063
$^3D - (^2S - ^2D)$	15306	-2097	-7090	-9359	-10649
$^3D - (^1S - ^1D)$	7106				

Russell and Saunders find that if 13711 ($^2S - ^2D$) be added to the sequence of 3P terms, they form approximately a Rydberg sequence.

Existence of 3F -terms.

The most important group of terms from the combination M_3M_3 is 3F , which is expected to be larger than 3P , identified with certainty with Russell and Saunders' p' . But these terms have not yet been identified. The cause is to be traced to its combinatory properties. It can combine with

$$^3F \quad ^1F \quad ^3D \quad ^1D$$

arising from combination (M_3M_2) and with the triplet F of the normal spectrum and also with the N_1N_2 terms (Ca). But the terms 3F , 1F , 3D , 1D of combination M_3N_2 have values very nearly equal to 3F , i.e. the difference $^3F - ^3F$ would be very small; the lines, if they exist, would be in the

far infra-red. Only in the case Ba can we expect 3F to have a sufficiently large value. We have not yet been able to identify the 3F terms without ambiguity, but the following identification may be provisionally given:—

	$\bar{F}_2(480.2)$ 19990.3	$\bar{F}_3(432.2)$ 19510.1	$\bar{F}_4$ 19077.9
$3^3F_2=7426.8$	(1u) 12563.5		
$3^3F_3=7412.8$	?	(2) 12097.3	(1r) 11665.4
$3^3F_4=7398.6$		(1) 12112.0	(6u) 11679.3

The combination with 3F of state $M_2 M_3$ ought to give us strong lines, but they would be hopelessly in the infra-red if these values of 3F prove to be correct. But we can take the higher Rydberg sequence terms of this 3F , for which Russell and Saunders give the values 4966.3, 4747.5, and 4558.6. We get the following multiplet:—

	$\bar{F}_2$ 19990.3	$\bar{F}_3$ 19510.1	$\bar{F}_4$ 19077.9
$2^3F_2=4966.3$	(1) 15024.1	(1) 14543.2	
$2^3F_3=4747.5$	?	(1) 14762.8	(1) 14330.5
$2^3F_4=4558.6$		?	?

Probably the last term, viz. 4558, has not been correctly identified, for we have failed to establish it from other sources. The reality of the 3F for Ba here given is strengthened by the following further combinations:—

$$\begin{aligned}
 19990.3 - q_1 &= 13305.2 \text{ (1u),} \\
 19510.1 - 3^1F_3 &= 13372.0 \text{ (2), } 19510.1 - q_2 = 12270.0 \text{ (2),} \\
 19510.1 - q_3 &= 12311.2 \text{ (2),} \\
 19077.9 - q_4 &= 11880.9 \text{ (1u).}
 \end{aligned}$$

Though the existence of the 3F terms has not yet been established, except in the case of Ba, they form very prominent members in the spectra of Sc^+ , Y^+ , and La^+ . Here $^2S - ^2D$ of M^+ (i.e. of Sc^{++} , Y^{++} , La^{++}) is negative, i.e. the 2D -term is larger than 2S ; hence terms which arise when the stationary electron is at M_3 are much larger than the terms arising out of the combination $N_1 X$: in other words, though the elements have a structure similar to that of the alkaline earths, the spectrum is just reversed, the anomalous terms become normal terms, and the normal terms become anomalous. Thus in Sc^+ ,¹⁸ for which the structure diagram is the same as that for Ca, we have the following terms (since the absolute value is not known, the largest term is given the value 0; the values of the other terms are obtained by subtracting the number placed against each number from the value of the biggest term:—

Sc ⁺		
State	Terms	Term values
$N_1 M_3$	3D 1D	0, 67.6, 177.8 ?
$M_2 M_3$	3F 3P	4802, 4883, 4987 12073.8, 12101.3, 12154.1
$M_3 N_3$	3F 3D 3P	27440.9, 27602.7, 27841.4 27918.1, 28021.6, 28161.5 ?

Thus here 3F forms the second biggest set of terms. The same feature is observed in the spectra of Y^+ and La^+ .¹⁹ The barium spectrum is intermediate in nature between the two groups Ca and Sr on one hand, Sc^+ , Y^+ , La^+ on the other hand.

¹⁸S. Goudsmit, J. van der Mark, and P. Zeeman, Proc. Amst. vol. xxviii. p. 127.

¹⁹ Y^+ -spectrum: Meggers, Journ. Opt. Sci. Am. vol. xii. p. 418 (1926). La^+ : Goudsmit, loc. cit. Goudsmit has apparently taken the terms in the reverse order.

40. A NOTE ON THE SPECTRUM OF NEON*

(Phil. Mag., Sr. VII, 4, 223, 1927)

Though the spectral lines of Neon have been completely grouped into series by Paschen, the nature of the series terms was not clearly understood, and a good deal of discussion has been devoted to it. Paschen¹ discovered

- A set of four terms ($s_2 s_3 s_4 s_5$)
- of value ranging between 38040—39887;
- a set of ten terms ($p_1 \dots p_{10}$)
- of value ranging between 20958—25671.65;
- a set of 12 terms ($d_1 d_1' \dots d_6, s_1', s_1'' \dots s''''$)
- of value ranging from 11493—12419.

None of these terms, however, constitute the fundamental level of Neon, which must have a very large value corresponding to the observed ionization potential of 21 volts. This level was discovered by Hertz², by means of his vacuum spectrograph. It gives rise to two lines $\lambda=735.7$ and $\lambda=743.5$, separated by a frequency interval of 1428, which is just the difference between the values of Paschen's s_2 and s_4 terms.

From these data, and from a discussion of data on the Zeeman effect of Neon-lines, Goudsmit³ has proposed the

*Communicated by the Author.

¹ Paschen, Ann. d. Physik, vol. lx, and lxiii.

²Hertz, Zs. für Physik, vol. xxxii. p. 933.

³See Goudsmit, Zs. f. Physik, vol. xxxii. and Back, vol. xxxvii.

following new designation of Paschen's terms. Goudsmit's schemes explains the structure of the Neon spectrum far better than Landé's theory of Spectra of the Second Degree (Spektra der Zweiter Stufe) which he deduced from his 'Verzweigungsprinzip.'

Terms (Paschen's Notation)	Designation according to Goudsmit	Observed <i>g</i> -factor.	Theoretical <i>g</i> -factor.
Hertz's funda- mental level.	1S_0	0/0	0/0
s_2	1P_1	1	1
s_3	3P	?	$\frac{8}{3}$
s_4	3P_1	$\frac{4}{3}$	$\frac{4}{3}$
s_5	3P_3	?	$\frac{8}{3}$
p_1	1S_0		$\frac{8}{3}$
p_5	1P_1	1	1
p_8	1D_2	1.137	1
p_{10}	3S_1	2	2
p_3	3P_0	?	$\frac{6}{5}$
p_2	3P_1	$\frac{4}{5}$	$\frac{6}{5}$
p_4	3P_2	$\frac{6}{5}$	$\frac{6}{5}$
p_7	3D_1	$\frac{3}{5}$	$\frac{1}{5}$
p_6	3D_3	$\frac{7}{5}$	$\frac{7}{5}$
p_9	3D_5	?	$\frac{4}{5}$

The nature of the next group of terms called *d*'s and *s*'s by Paschen has been fixed up by Hund, though their *g*-factor is yet unknown. Most of the lines arising from the combination of these terms with the *p*'s lie in the extreme infra red, so that it would be very difficult to observe their Zeeman effect. It is, however, evident that

they cannot all belong to the *d* group, for d_6 has the inner quantum number 4, and no triplet term up to *d* can have such a high inner quantum number. Higher terms like 3F are clearly involved. In this note, the above facts discovered by Hund and Goudsmit are put in new symbols explained by the author in an earlier paper (Saha, Phil. Mag., June 1927).

The number below each term like M denotes the full number of electrons required to close the subgroup completely. A level like L_2 was subdivided into L_{21} , L_{22} , by Stoner with two and four electrons respectively, but this has been omitted.

Advantage of this Method of Representation.

The first period Li to Ne ... is formed when the electrons are made to fill the L-levels. The second period (11) Na to (19) A when the M, and M_2 levels are filled up. It is now known, that if a fresh electron is now brought up, instead of going to M_3 , it comes over to N_1 , forming K and Ca.

The negative energy value of the electron in position N_1 is therefore larger than the value in position M_3 . To represent this state of affairs, we have written N_1 below M_2 and not following M_3 , as is usually the custom. We have followed this system all throughout. Thus roughly if by (X) we represent the energy value of any level, then

$$\begin{aligned}
 (K_1) &> L_1 > (L_2), (M_1) \\
 &> (M_2), (N_1) \\
 &> (M_3), (N_2), (O_1) \\
 &\text{etc., etc.}
 \end{aligned}$$

Chart illustrating the Formation of Atoms.

H	K ₁				Transition I 21 Sc to 28 Ni	Group II 39 V to 46 Pa	Rare Earths 57 La to 70 Yb	Transition Group III 71 Lu to 78 Pt			
He	2										
3 Li to 10 Ne		L ₁ 2	L ₂ 6								
11 Na to 18 A			M ₁ 2	M ₂ 6	M ₃ 10						
29 Cu to 36 Kr		19 K 20 Ca		N ₁ 2	N ₂ 6	N ₃ 10	N ₄ 14				
47 Ag to 54 Xc		37 Rb 38 Sr			O ₁ 2	O ₂ 6	O ₃ 10	O ₄	O ₅		
79 Au to 86 Nt		55 Ca 56 Ba				P ₁ 2	P ₂ 6	P ₃	P ₄	P ₅	P ₆

Terms on the same vertical column like (L_2) (N_1) or (M_3) (N_2) (O_1)... have the same order of energy value, though each preceding term is larger than the next.

The diagram makes clear the formation of the transitional groups, and rare earths, and persistence of the pair of alkali and alkaline earths throughout the whole system. After Argon, we have K and Ca formed in which the N_1 -level is filled up. The next electron must go to the M_3 -level. This happens till the M_3 -level is completely filled up. Then with copper, a new group begins to be formed. In this way, we can explain the formation of pairs of alkalies and alkaline earth (O_1 —Rb and Sr), (P_1 —Cs and Ba), the successive transitional groups, and the rare earths.

Application to Spectroscopy.

But the scheme is more fruitful when we utilize it for the explanation of spectra:—

Taking Na, we again write out the structure diagram, but now with the higher levels unfilled:—

Spectrum of Sodium.

K_1 2	L_1 2	L_2 6					
		M_1 (1)	M_2 (1)	M_3 (1)			
		2S	2P	1D			
			N_1 (1)	N_2 (1)	N_3 (1)	N_4 (1)	
			2^2S	2^2P	2^1D	1^2F	

M_1 L denotes the normal level of the atom. It is the first term of the S-series, and may be written as 1^2S_1 , using Russell and Saunders' notation. The electron, as it runs through the higher levels denoted by (1), gives rise to the spectral terms written under that level. The diagram also gives a rough indication of the sequence of values of successive terms. Thus

$$1^2S_1 > 1^2P_{1,2}, 2^2S \\ > 1^2D_{2,3}, 2^2P_{1,2}, 3^2S_1 \\ > 1^2F_{3,4}, 2^2D_{2,3}, 3^2P_{1,2}, 4^2S.$$

Of course these inequalities are only roughly obeyed.

In the construction of the spectra of alkaline earths, we have to keep one electron fixed at N_1 , O_1 or P_1 , as the case may be and allow the other electron to run through the higher levels. The methods of working have already been discussed in a previous paper communicated to the Philosophical Magazine.

We shall now discuss the spectrum of Neon.

Explanation of the Spectrum of Neon.

K_1 2	L_1 2	L_2 5, 1					
		M_1 (1)	M_2 (1)	M_3 (1)			
			N_1 (1)	N_2 (1)	N_3 (1)	N (1)	
			O_1 (1)	O_2 (1)	O_3 (1)	O_4 (1)	

The normal state of Neon is obtained when all the six electrons are allowed to fill the L_2 -level. It has got $I_k=0$, $I_r=0$, hence it is an 1^2S_0 -term.

The higher orbits are produced when we keep 5 electrons in L_2 and allow the other to pass through the higher levels. The 5 electrons in L_2 give us a doublet P-level, so that we can construct the terms successively as follows:—

$$\begin{array}{l} \text{Running electron} \\ \text{in } M_1 \end{array} \left\{ \begin{array}{l} \text{Combination of } ^2P \text{ with } ^2S_1 \\ I_r = \frac{3}{2}, 0, I_k = |1+0| = 1. \end{array} \right.$$

Hence we get 1^2P_1 , $3^2P_{0,1,2}$ which are identified by Goudsmit with Paschen's s_2 , s_3 , s_4 , s_5 .

If the running electron is in N_1 , O_1 , P_1, we shall get the higher Rydberg sequences of these terms.

$$\begin{array}{l} \text{Running electron} \\ \text{in } M_2 \end{array} \left\{ \begin{array}{l} \text{Combination of } ^2P \text{ with } ^2P \\ I_k = |1+1| = 2, 1, 0. \end{array} \right.$$

Hence we expect

$$\begin{array}{ll} c^1S_0 & c^3S_1, \\ c^1P_1 & c^3P_{0,1,2}, \\ c^1D_2 & c^3D_{1,2,3}. \end{array}$$

These are the terms which have been obtained by Goudsmit by a similar process, and identified with Paschen's p 's. Now it is quite evident that the p -terms arising from this process will be capable of combining with the previous p -terms (Paschen's s 's). For the process simply means transition of the electron from $M_1 \rightarrow M_2$ and it is perfectly admissible. The present p -terms must therefore be dashed, while the s - and d -terms must remain undashed.

Since all these terms arise from the same level, they have approximately the same scale of values, as observed.

If the electron is in any one of the higher 2-levels, as N_2 or D_2 , or P_2 , they will give rise to the higher Rydberg sequences to the present set, having identical combinatory powers.

$$\begin{array}{l} \text{Running electron} \\ \text{in } M_3 \end{array} \left\{ \begin{array}{l} \text{Combination of } ^2P \text{ with } ^2D. \\ \text{We have } I_k = |2+1| = 3, 2, 1. \end{array} \right.$$

Hence we expect

$$\begin{array}{ll} d^1P_1 & d^3P_{0,1,2}, \\ d^1D_2 & d^3D_{1,2,3}, \\ d^1F_3 & d^3F_{2,3,4}, \end{array}$$

We expect twelve terms.

Now Paschen has given exactly twelve terms with

$$\begin{array}{ll} j=0, \text{ for } d_6 & \therefore d_6 = c^3P_0 \\ j=1, \text{ for } (d_2 d_5 s_1') & = (c^1P_1, c^3P_1, c^3D_1), \\ j=2, \text{ for } (d_1'' d_3 s_1'' s_1''') & = (c^1D_2, c^3P_2, c^3D_2, c^3F_2), \\ j=3, \text{ for } (d_1', d_4, s_1''') & = (c^1F_3, c^3D_3, c^3F_3), \\ j=4, \text{ for } d_4^1 & = c^3F_4. \end{array}$$

The explanation of these terms is due to Hund, but detailed identification is difficult, and an attempt has been made by writing down the multiplets and comparing the intensities according to that to be expected from the

Sommerfeld-Ornstein-Dorgelo scheme. Table I shows the results of detailed identification.

Spectral Term	Term in Paschen's notation	Term Values	Inner Quantum Number
d^1P_1	s_1'	11493.76	1
$*d^1\bar{D}_2$	d_1''	12229.69	2
$\dagger d^1F_3$	s_1'''	11519.27	3
d^3P_0	d_0	12419.90	0
3P_1	d_5	12405.20	1
3P_2	d_3	12322.24	2
$d^3\bar{D}_1$	d_4	12292.98	1
$*d^3\bar{D}_2$	s_1''	11509.52	2
$d^3\bar{D}_3$	d_1'	12228.26	3
$\dagger d^3F_2$	s_1''''	11520.80	2
d^3F_3	d_4	12337.35	3
d^3F_4	d_4'	12339.15	4

*The positions of these two terms may be interchanged.

†Positions interchangeable.

The identification is somewhat ambiguous in certain cases. How far the intensity rules are followed will be seen from the following tables. Certain values like $(d_1' d_1'')$ are so close to each other that the lines occurring from them cannot be separated from each other, and the intensity-data in these cases are open to certain amount of doubt. The values of all these terms are of the same order and approximately equal to $\frac{N}{3^2}$. Some of the multiplets with intensities are shown in the following tables.

TABLE II
The c^3D-d^3F -multiplet

$c=5L_2M_2$ $d=5L_2M_3$	(p_7) 3D_1	(p_6) 3D_2	(p_5) 3D_3
$(s''')^3F_2$	8136.4 (7) 12287.0	8267.14 (3) 12092.7	
$(d_4)^3F_3$		8865.7 (3) 11276.3	8376.4 (1) 11934.9
$(d_4')^3F_4$			8377.63 (7) 11933.3
$(d_0)^3P_0$	5934.46 (7) 16846.0		
$(d_5)^3P_1$	?	6000.95 (6) 16659.4	
$(d_3)^3P_2$	5919.04 (2) 16889.9	5987.93 (8) 16695.6	5760.58 (7) 17354.5

The multiplet represents the combination of 3D , and second Rydberg sequence of 3P terms.

The $c^3D-d^3\bar{D}$ -multiplet

c d	(p_7) 3D_1	(p_6) 3D_2	(p_5) 3D_3
$(d_2)^3\bar{D}_1$	8681.93 (3) 11515.0	8830.80 (0) 11320.9	
$(s_1'')^3\bar{D}_2$	8128.95 (3) 12298.3	8259.39 (4) 12104.1	7833.12 (1) 12762.8
$(d_1')^3\bar{D}_3$		8780.63 (4) 11385.6	8300.34 (7) 12044.4

Singlet-Combinations

c d	p_{10} S_1
$(s_1')^1P_1$	7051.29 (5) 14177.9
$(d_0)^3P_0$	7544.08 (6) 13251.8
$(d_5)^3P_1$	7535.78 (8) 13266.4
$(d_3)^3P_2$	7488.85 (9) 13349.5
$d_4)^3\bar{D}_1$	7472.42 (4) 13378.8

It will thus be seen that the complicated spectrum of Neon is very simply explained on the recent theories of complicated spectra. The theory accounts for not only the fundamental levels, but also for all the higher levels, the Rydberg sequences, and the order of values observed in each case. It also gives a very cogent explanation of the origin of the dashed terms, and explains such transitions as apparently break the selection principle, *e.g.* $\Delta K=2$, or 3.

We can summarize the results as follows:—

Position	Term
(a) $6L_2$,	1S_0
(b) $5L_2, M_1$ N_1	$^1P_1, ^3P_{0,1,2}$ Higher Rydberg sequence terms to the above.
(c) $5L_2, M_2$	b^1S_0 b^3S_1 b^1P_1 $b^3P_{0,1,2}$ b^1D_2 $b^3D_{1,2,3}$
$5L_2, N_2$ } O_2 }	Same terms but of higher Rydberg sequence.
(d) $5L_2, M_3$	$^1cP^1$ $^3cP_{0,1,2}$ c^1D_2 $c^3D_{1,2,3}$ c^1F_3 $c^3F_{2,3,4}$
$5L_2, N_3$ } O_3 }	Gives higher Rydberg sequence terms.

Transitions take place between terms of groups

$$(a) \rightarrow (b) \rightarrow (c) \rightarrow (d) \rightarrow$$

Corresponding to the transition of the electron from

$$L_2 \rightarrow M_1 \rightarrow M_2 \rightarrow M_3$$

The scheme also explains that the fundamental term 1S_0 will be rather solitary, *i.e.* will not have terms of higher Rydberg sequence following it.

My thanks are due to Mr. K. Mazumder for drawing the charts.

41. ON THE EXPLANATION OF COMPLICATED SPECTRA OF ELEMENTS

(Estratto dagli Atti del congresso Internazionale dei Fisici Como-
Settembre 1927(V))

During the whole of the last century the belief was almost universal that the atom was an indivisible particle of mass with certain combining powers. This belief is now completely shattered owing to the discovery of the proton and the electron, and recognition of the fact that all elements are made up of these primordial elements. But the first suspicion on the indivisibility of the atom was thrown from studies on spectroscopy, in which it was found that even the simplest element viz. hydrogen does not give a single line, but apparently a fairly large number of lines. An element like iron gives in the visible range not less than 6000 lines. This fact led Rowland to remark that the atom is more complicated than even a grand piano.

It is not so well-known that long before the discovery of the electron, Sir Norman Lockyer, guided by his experience on the spectrum of different classes of stars, put forward the hypothesis of protoelements and subatomic particles. Prof. A. Fowler (1) informs us that Lockyer performed thousands of experiments to break up the elements by purely electrical discharge. The elements were indeed being broken up, but Bohr's theory had not yet appeared, and he had no means of interpreting his results. Icarus-like were his attempts and their significance was quite unappreciated at his own times.

The spectrum is the most characteristic property of the atom, and it was perceived long ago that the proper interpretation of spectroscopic data is the key to the progress of atomic physics. But the task of interpretation is not so simple. Ever since the discovery of spectrum analysis by Kirchhoff about seventy years ago, spectroscopic data are accumulating such quantity that even the seven thick volumes of Kayser and Runge, and Konen are barely sufficient for reporting all the results. The vastness of the data combined with their complexity repelled even the greatest physicists of the last century against such an attempt. A great physicist once declared that he did not wish to engulf himself in the bog of spectroscopy.

The various steps by which a better understanding of spectroscopic data has been arrived at are now well-known. The first great landmark was Balmer's discovery of regularity in the hydrogen spectrum. Close upon this, followed the researches of Rydberg and Ritz on the alkali-spectrum, the discovery of the principle of combination and of the universal Rydberg constant. While the work of systematisation of spectroscopic data was being continued by Fowler

and Paschen, there appeared in 1912, the epochmaking work of Bohr on the hydrogen spectrum, which gave the first Rutherford's atomic model; it also opened a general way for the interpretation of spectra. After Bohr's work, progress has been more rapid, and we can notice the following chief landmarks: Sommerfeld's generalisation of Bohr's theory (2), and the introduction of the various quantum number, n, k, j, r, m ; Sommerfeld and Kossel's displacement law (3); Catalan's discovery of multiplets (4); Landé's theory of Zeeman effect (5). The gradual clearing of our ideas on the electronic composition of atoms in the hands of Bohr, Stoner and Mainsmith; Pauli's principle of exclusion, and recognition of the fact that the doublet (or alkali type of) spectrum is the fundamental type (6). Pauli, Russell, Saunders (7) and Heisenberg's (8) principle of orbit or term synthesis. Utilising these principles, Hund (9) has achieved the apparently impossible task of explaining the whole data in complex spectra. Simultaneously a new quantum-mechanics has arisen in which, though much is still obscure, it is sure that a new way has been opened in the investigation of the atomic world. This is the wave-mechanics of De-Broglie-Schrödinger (10) with which the matrix-mechanics of Heisenberg, Born and Jordan (11) and the non-commutative mechanics of Dirac (12) are associated. We have also come to recognise that the electron is not merely a point-charge of electricity, but is also probably the fundamental magnetic unit—a fact which was first clearly stated by Goudsmit and Uhlenbeck (13). On the experimental side, we must mention the works of Millikan and Bowen who by applying the irregular doublet law, have very largely extended our knowledge of spectra of stripped atoms in the Schumann region.

The mechanical interpretation of spectra begun by Bohr and continued by Sommerfeld and others is however changing in a perplexing, rather kaleidoscopic way within the last few years. With Bohr, we believed in nonradiating orbits and quantum transitions. In Sommerfeld's generalisation not less than four quantum numbers had to be introduced to account for complex spectra, and were interpreted in terms of different mechanical quantities. Thus taking the symbol n^r_{kf} , to denote a spectral term, according to Sommerfeld,

n = total quantum number (i.e. energy of the orbit
approximately $= -R \frac{(z-s)^2}{n^2}$.

k = azimuthal quantum number 1, 2, 3, 4, for s, p, d, f orbits.

r = multiplicity quantum number, denoting the resultant magnetic moment of the atomic residue (rest of the atom minus the valence electron) 1, 2, 3, 4 for singlets, doublets, triplets, etc.

j = inner quantum number, defining the total magnetic moment of the atom which consists of magnetism due to the atomic residue plus magnetism due to the orbital motion of the valence electron. j is thus the vector sum of k and r .¹

m = magnetic quantum, and is simply the quantumlike projection of j on a definite axis in space.

¹ It is not yet clear how this magnetism arises. The idea of spinning introduced by Goudsmit and Uhlenbeck is merely symbolic. An attempt of Einstein to explain the existence of the electron from considerations of the theory of relativity has not yet borne fruit. (Einstein: Berl. Sitzungsberichte 1925). See also a discussion in "Nature", Vol. 116, p. 316.

It has been found that though all these quantum numbers (and probably more) e.g. five quantum numbers are required to describe an optical term completely, the mechanical interpretation put on these numbers is not always certain. In the original Bohr-Sommerfeld theory, all the quantum numbers were integral; gradually from study of Band spectra and Zeeman effect, half quantum numbers had to be introduced. Even before the rise of wave mechanics, it was found necessary to introduce associated quantum number. Thus instead of k , we now use i_k ,

$$i_k = 0, 1, 2, 3 \text{ for } s, p, d \text{ and } f\text{-orbits}$$

which shows that an atom in the s -state (rather) has no magnetic moment, i.e. the first s -state say of hydrogen, does not correspond to an electron revolving in a circular orbit, but to a state inexpressible in ordinary mechanical terms; the magnetic moment being zero.

CHART I.

K ₁				Transitional group I	Transitional group II	Rare earths	Transitional group III
1 H	2						
2 He							
3 Li ... L ₁				21 Sc M ₃ 2N ₁ , 2M ₂ N ₁	39 V 2N ₂ O ₁ , N ₂ 2O ₁	57 La	
4 Be ... 2L ₁	L ₁	L ₂		22 Ti 2M ₂ 2N ₁ , 3M ₂ N ₁	40 Zn 3N ₂ O ₁ , 2N ₂ 2O ₁	58 Ce	89 Ac
5 B ... L ₁				23 V 3M ₂ 2N ₁ , 4M ₂ N ₁	41 Nb 4N ₂ O ₁ , 3N ₂ 2O ₁	59 Pr	90
6 C ... 2L ₁	2	6		24 Cr 5M ₂ N ₁ , 4M ₂ 2N ₁	42 Mg 5N ₂ O ₁ , 4N ₂ 2O ₁	60 Nd	91 Pa
7 N ... 3L ₁				25 Mn 5M ₂ 2N ₁ , 6M ₂ N ₁	43 Tc	61	92 Ur
8 O ... 4L ₁				26 Fe 6M ₂ 2N ₁ , 7M ₂ N ₁	44 Ru 6N ₂ 2O ₁ , 7N ₂ O ₁	62 Sm	
9 F ... 5L ₁				27 Co 7M ₂ 2N ₁ , 8M ₂ N ₁	45 Rh 8N ₂ O ₁ , 7N ₂ 2O ₁	63 Eu	
10 Ne ... 8L ₁				28 Ni 8M ₂ 2N ₁ , 9M ₂ N ₁	46 Pd 10N ₂ , 9N ₂ O ₁	64 Gd	
11 Na ... M ₁		M ₁	M ₂			65 Tb	
12 Mg ... 2M ₁		2	6			66 Dy	
13 Al ... M ₁						67 Ho	
14 Si ... 2M ₁						68 Er	
15 P ... 3M ₁						69 Yb	
16 S ... 4M ₁							
17 Cl ... 5M ₁							
18 Ar ... 6M ₁							
19 K ... 6M ₁ N ₁							
20 Ca ... 6M ₁ 2N ₁							
21 Sc ... 10M ₁ N ₁ 9M ₂ 2N ₁							
22 Ti ... 2N ₁							
23 V ... N ₁							
24 Cr ... 2N ₁							
25 Mn ... 3N ₁							
26 Fe ... 4N ₁							
27 Co ... 5N ₁							
28 Ni ... 6N ₁							
29 Cu ... 10N ₁ O ₁							
30 Zn ... 2O ₁							
31 Ga ... O ₁							
32 Ge ... 2O ₁							
33 As ... 3O ₁							
34 Se ... 4O ₁							
35 Br ... 5O ₁							
36 Kr ... 6O ₁							
37 Rb ... 6N ₁ O ₁							
38 Sr ... 6N ₁ 2O ₁							
39 Y ... 10N ₁ O ₁							
40 Zr ... 2O ₁							
41 Nb ... O ₁							
42 Mo ... 2O ₁							
43 Tc ... 3O ₁							
44 Ru ... 4O ₁							
45 Rh ... 5O ₁							
46 Pd ... 6O ₁							
47 Ag ... 10N ₁ O ₁							
48 Cd ... 2O ₁							
49 In ... O ₁							
50 Sn ... 2O ₁							
51 Sb ... 3O ₁							
52 Te ... 4O ₁							
53 I ... 5O ₁							
54 Xe ... 6O ₁							
55 Cs ... 6O ₁ P ₁							
56 Ba ... 6O ₁ 2P ₁							
57 La ... 10N ₁ O ₁							
58 Ce ... 2O ₁							
59 Pr ... O ₁							
60 Nd ... 2O ₁							
61 Pm ... 3O ₁							
62 Sm ... 4O ₁							
63 Eu ... 5O ₁							
64 Gd ... 6O ₁							
65 Tb ... 10N ₁ O ₁							
66 Dy ... 2O ₁							
67 Ho ... O ₁							
68 Er ... 2O ₁							
69 Yb ... 3O ₁							
70 Lu ... 4O ₁							
71 Lu ... 6O ₁							
72 Hf ... 10N ₁ O ₁							
73 Ta ... 2O ₁							
74 W ... O ₁							
75 Re ... 2O ₁							
76 Os ... 3O ₁							
77 Ir ... 4O ₁							
78 Pt ... 5O ₁							
79 Au ... 6O ₁							
80 Hg ... 10N ₁ O ₁							
81 Tl ... 2O ₁							
82 Pb ... O ₁							
83 Bi ... 2O ₁							
84 Po ... 3O ₁							
85 At ... 4O ₁							
86 Rn ... 5O ₁							
87 Rad Cs ... O ₁							
88 Ra ... 2O ₁							
89 Ac ... 3O ₁							
90 Th ... 4O ₁							
91 Pa ... 5O ₁							
92 U ... 6O ₁							

Similarly the mechanical interpretation put on the other quantum numbers has to be changed, and the meaning of some of them are still a bit mysterious.

Owing to the uncertainty in the meaning of the quantum numbers, I have attempted to present Hund's interpretation of spectra in terms of quantum numbers alone, dispensing with the mechanical analogy as much as possible (it is often impossible to do so). The main innovation consists in the introduction of a new atomic chart illustrating the electronic composition of atoms. It ought to be mentioned that the chart has been evolved out of the original conceptions of Bohr and Mainsmith-Stoner. It gives in one diagram a graphical representation of the origin of X-ray spectra, the periodic classification of elements, and origin of optical spectra. No new principles have been evolved, but principles already discovered have been represented in a new way.

On the Electronic Composition of Atoms.

Explanation of the Chart.—For an understanding of the chart, let us consider how the element with the atomic number N is built up. We have in the centre a nucleus with the positive charge N . We have to bring up N electrons about it one by one. These electrons take their position in different levels possessing definite quantummechanical

characteristics. These levels are graphically shown in chart 1. They are first differentiated according to their total quantum number n . The innermost level K , has $n=1$, (mechanically, it roughly signifies that if an electron is in the K -orbit, it will have the energy $= -R \frac{(z-1)^2}{1^2}$). The K -level is single.

For the next level, $n=2$, and they are denoted by L . X-ray absorption experiments however show that the L -level is apparently triple i.e. consists of three sublevels. These were designated by L_{11} , L_{21} , L_{22} (here instead of L_{21} we write L_2 ; L_{31} , L_{22} are combined under L_2).

For the next level, $n=3$, and they are denoted by M . M is apparently quintuple, and the sublevels are denoted by M_{11} , M_{21} , M_{22} , M_{32} , M_{33} (denoted by M_1 , M_2 , M_3 in the chart).

We have now to explain the subscripts. They were introduced to explain the observed combinations and a perfect analogy which was discovered by Pauli between the X-ray levels, and the optical levels of the valency electron in alkali-spectrum say, in the spectrum of Na. As this analogy is of far-reaching importance, we shall dwell upon it more in detail. The optical terms of Na with their n , k , j -values are shown in diagram 1.

Bohr Russell
Saunders

Optical Terms of Na

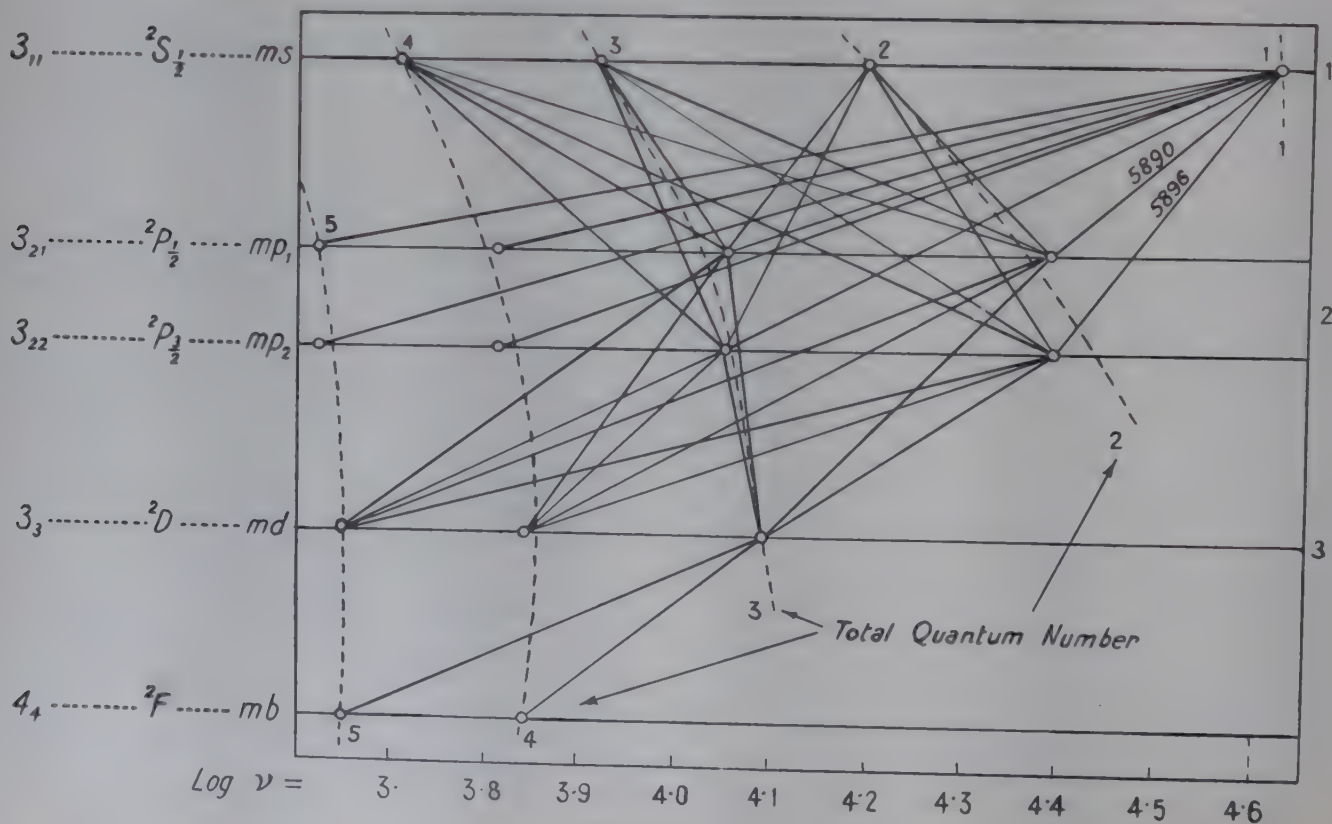


Diagram 1.

In the spectrum of Na, the fundamental level is a doublet S -term, for which $k=1$, $j=1$, $n=1$ according to the Sommerfeld-Landé notation. We can also designate the term according to the new notation introduced by Saunders and Russell. Then this would be written as $1\ ^2S_1$ (first term of the doublet S -series, with $j=1$). This term is followed by its Rydberg sequence for which n varies from 2, 3, ... They are shown in diagram 1), in the Saunders-Russell notation.

The next family is the doublet p -series, for which $k=2$, and each term is double. This fact is expressed by introducing a new quantum number j , and giving it the values 1 and 2 for the two terms respectively. The chief quantum number n begins with 2.

Then follows the doublet d -series, having $k=3$, $j=2$, 3 and n beginning with 3.

We therefore see that in the spectrum of Na, we can thus differentiate amongst the different groups of terms according to their chief quantum numbers.

(1) $n=1$; there is only one term $1\ ^2S_1$... analogous to K_1 in the chart 1).

(2) $n=2$; there are three terms
 $2\ ^3S_1$, $\overbrace{3\ ^2P_1\ ^2P_2}$

Corresponding to L_1 , L_2 in chart (1).

(3) $n=3$; there are five terms
 $3\ ^2S_1$, $\overbrace{3\ ^2P_1\ ^2P_2}$, $\overbrace{3\ ^2D_2\ 3\ ^2D_3}$

corresponding to M_1 , M_2 , M_3 in chart (1).

The analogy is complete not only as regards n -values, but also as regards the k and j values; r is of course always=2. This perfect correspondence of the quantum-mechanical values for the two diagrams is derived from the observed combinations, and the particular k , j -values were assigned to the different levels to explain the combinations. We can say that the atomic chart(1) is simply the diagram(1) written in a slightly different form, and with slightly different meaning for each level.

The difference in the significance of the corresponding levels, say L_2 , and 2P is easily grasped. The optical levels of Na correspond to the position of the outermost electron when this is excited. The various K , L , M -levels in the chart indicate the quantum mechanical characteristics of any constituent electron, inner or outer, as they are brought up to build up the atom. The analogy suggests a periodicity, or reoccurrence of levels with the same quantum characteristics and this recurrence is at the basis of the quantum explanation of the periodic classification of elements, and periodicity in the structure of spectra. The periodicity is apparent from chart (1). Thus

(1) K_1 , L_1 , M_1 ... i.e. all levels lying along the first

diagonal with the same subscript, 1, impart to the electrons contained in them, the same quantum characteristics as are possessed by the 2S_1 -term of alkalis. They differ only in the n -values. The electrons lying in such levels may for the sake of brevity be called s -electrons.

(2) L_2 , M_2 , N_2 ... i.e. all levels lying along the second diagonal with the subscript, 2, impart to the electrons contained in them the same quantum characteristics as are possessed by the P -terms of alkalis. The n -values begin from 2 (for L_2). The electrons lying in such levels may be called p -electrons.

Similarly electrons under M_3 or X_3 may be called d -electrons.

Let us now make the very important assumption—in fact an assumption which includes the whole significance of the present paper—that whatever the charge on the atomic nucleus may be, *the levels shown in chart 1) are always potentially present*. We have to make the further assumption that the levels can contain a maximum number of electrons, which is definite for each level. These numbers were first correctly given by Stoner, and explained by Pauli (13) on the basis of his famous principle of exclusion (Paulische Verbot). These numbers are 2 for an s -level (K , L ...), 6 for a p -level (L , M ...), 10 for a d -level (M , N ...) as indicated in the chart 1).

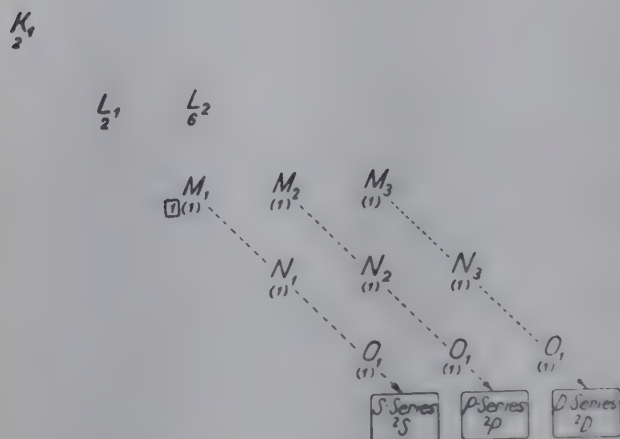
There are many points in the above sketch which will appear quite mysterious at the first reading. But without trying to lift up the mystery at this point, we shall follow the chart to its logical consequence. A glance at the chart shows that it affords a satisfactory explanation of the grouping of elements with periodic repetitions of chemical and physical properties, if we suppose *that these properties depend entirely upon the constitution of the outermost shells*. The closed groups are chemically inert, e.g. He, Ne, or A In Li, Na, K, Rb and Cs ... there is only one s -electron outside of the closed groups, and hence they possess identical chemical properties. We shall return to this point later on. Let us now see how the spectra of elements can be explained from the atomic chart.

For this, we have to follow the assertion made previously "*whatever the charge on the atomic nucleus may be, the levels shown in chart 1) are always potentially present*" to its logical consequence. This leads us to the following rules for.

The Deduction of the Nature of the Spectrum from the Atomic Chart.—Write out the K , L ... levels as in the atomic chart and below each write out the full number of electrons. Stop when the number of electrons is equal to the atomic number. Then take the last electron, and make it run through the higher unfilled levels. We get all the optical terms.

As the simplest case we take Na. We have the structure diagram shown below.

STRUCTURE DIAGRAM OF Na



Sodium contains 11 electrons. Of these 2 fill up the K-level and 8 the L-levels completely. The remaining electron is normally at M_1 ... the normal level is 2S_1 . The next transitions are shown by the symbol (1). We get successively the 2P , 3D -terms. All terms arising from a diagonal displacement from the successive numbers of a Rydberg sequence. This is indicated in the structure diagram. If we take any other alkali element, say Li, K, Rb or Cs, we find the same story repeated.

Rules of Transition.—We know that the s -terms can combine with p -terms only, and cannot generally combine with another s -term or a d -term. To come from a s -term to a p -term, we must displace the electron (horizontally or vertically both being regarded equal; but not diagonally) an odd number of times. To come from an s -term to another s -term or d -term, the number of displacements required is even. So we may formulate a general principle:—*Only such transitions of the electron are possible which involve an odd number of displacements. An even number of displacements is forbidden.*

We shall see that this rule is of universal application.

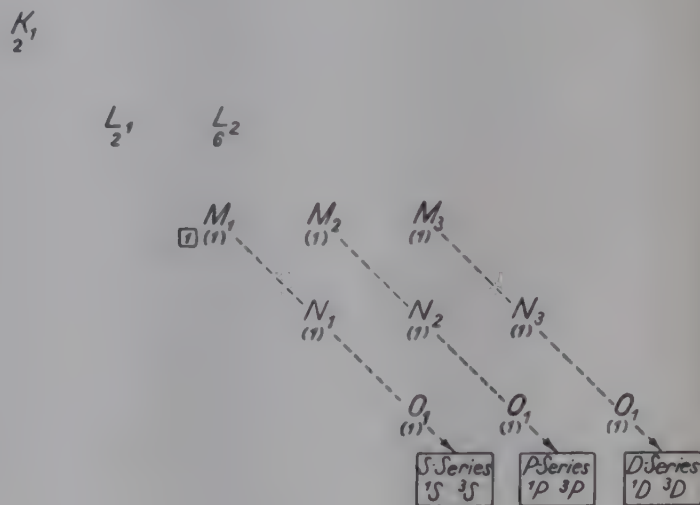
The Hydrogen Spectrum.—The hydrogen spectrum being the simplest, it would have been rather disconcerting if its spectrum did not correspond to the fundamental doublet type as it will be according to the rule given above. Landé was the first to show that the optical levels of hydrogen correspond in every respect to the levels of the alkali spectra and this fact was later elucidated by Goudsmit and Uhlenbeck, and Sommerfeld and Unsöld (15). There are therefore one set of s -terms, a double set of p -terms, a double set of d -terms. For practical purposes, the first two double sets of p -terms need be considered because the other differences are rather too small. The fine structure of hydrogen lines is therefore not due to relativity-effect, but arises from the same cause as in the alkalis.

Spectra of Two Valence Elements.—Under the heading, we include the spectra of He, Be, Mg, Zn, Cd, Ca, Sr, Ba.

But for the sake of convenience, we shall begin with the spectrum of Mg. Let us write out the structure diagram.

We see that after the K and L-levels have been completed, there are two electrons at M_1 . The normal orbit of Mg arises when both electrons are at M , the higher terms arise when one is kept permanently at M_1 , the other is allowed to run through the higher levels.

STRUCTURE DIAGRAM OF Mg



Let us now write out the term-levels of Mg. We are reproducing actually the term-scheme of Hg from ((Handbuch der Physik)), Band 23, (Quanten). The two term schemes are essentially the same, only in Hg, the P , and D -separations are much larger, and hence the scheme is shown to greater advantage (Diagram 2).

They consist of a set of singlet terms and triplet terms. The singlet terms consist of a sequence of s -terms, beginning with the chief quantum number 1; a set of P -terms beginning with $n=2$; a set of D -terms beginning with $n=3$.

The triplet terms consist of a sequence of s -terms beginning with $n=2$; a set of P -terms beginning with $n=2$, etc.

The first S -term of the singlet system is the normal term.

Looking at the structure diagram, we can assign the following origin for the different groups of terms:

- $M_1 M_1$ (both electrons at M) gives 1S_0 (first term of s -sequence);
- $M N$ (one fixed electron at M , running electron at N)
 $2^1 S_0, 2^3 S_1$;
- $M X_1$ (two fixed electrons at M , running electron at X) $x^1 S_0, x^3 S_1$.

For the P -terms:

- $M_1 M_2$ (one electron fixed at M_1 , running electron at M_2) gives $2^1 P, 2^3 P$ -terms.

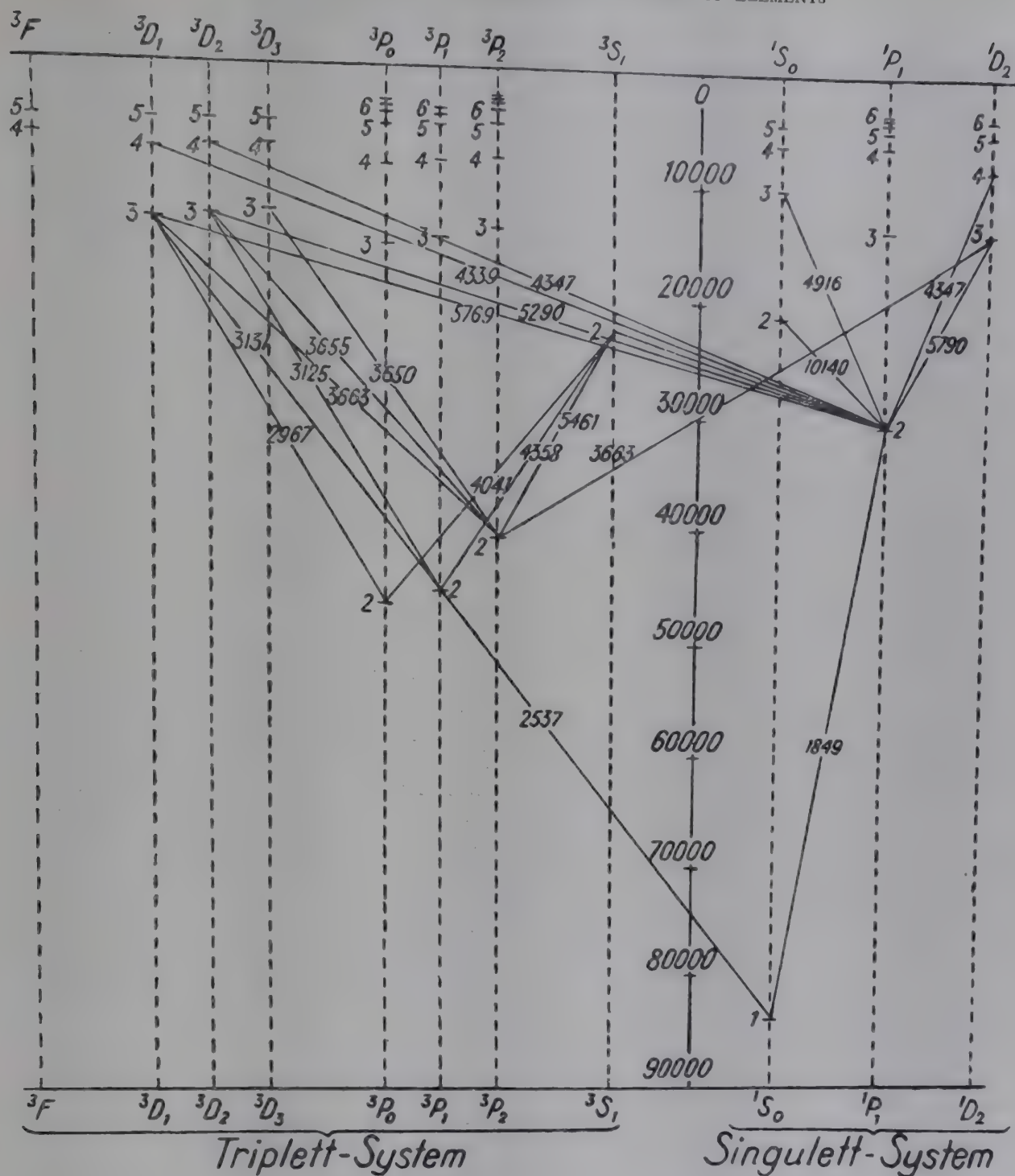


Diagram 2.

Similarly the D -set is obtained when the running electron is allowed to run through the X_3 levels. They are symbolically shown in the structure diagram.

The question now arises: how are we to explain the origin of terms? Why in the normal position, we get only the singlet S -terms, and why is the triplet term missing?

The answer was first given by Pauli and further elucidated and generalised by Russell and Saunders, and Heisenberg. Let us suppose that the electrons in the atom have the characteristics of a doublet term. Thus $M_1 M_1$ denotes

that both electrons have the characteristics of doublet S -terms, i.e. 2S_1 . $M_1 M_3$ denotes that the first electron has the characteristics of a doublet S -term, the second of a doublet D -term (the subscription 1 stands for S -term, 2 stands for P -term, 3 for D -term, etc.). The resultant term is obtained when the quantum numbers of each constituent terms are added, vectorially.

Rules for Addition of Quantum Numbers.—These rules for the vectorial addition of quantum numbers are a bit

perplexing. We have already remarked that according to Landé and Sommerfeld, each optical term can be represented by n^j_{kr} , where n =total quantum number, r =multiplicity quantum number, k =azimuthal quantum number, j =inner quantum number.

Now instead of using Landé's values of r, k, j for the different systems, we use Sommerfeld's values, which we denote by i_r, i_k, i_j .

$$\text{Now } i_r=0, \quad \frac{1}{2}, \quad \frac{2}{2}, \quad \frac{3}{2} \quad \dots$$

for singlets, doublets, triplets, quartets etc., respectively.

r =usual Landé multiplicity quantum number

$$i_k=0, 1, 2, 3$$

for s, p, d, f -term, $i_k=k-1$

i_j =the vector sum of i_r and i_k , and the i_j -values for the different multiplet systems are shown in the Table 1.

TABLE 1.—Showing values of i_r, i_k, i_j

ODD MULTIPLETS							EVEN MULTIPLETS						
i_j i_k	0	1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	i_j i_k	
$s=0$	0	Singlet $i_r=0$					$\frac{1}{2}$	Doublet $i_r=\frac{1}{2}$				$s=0$	
$p=1$		1					$\frac{1}{2}$	$\frac{3}{2}$				$p=1$	
$d=2$			2				$\frac{3}{2}$	$\frac{5}{2}$				$d=2$	
$f=3$				3			$\frac{5}{2}$	$\frac{7}{2}$				$f=3$	
$s=0$		1	Triplet $i_r=\frac{2}{2}$				$\frac{3}{2}$	Quartet $i_r=\frac{3}{2}$			$s=0$		
$p=1$	0	1	2				$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$			$p=1$	
$d=2$		1	2	3			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$		$d=2$	
$f=3$			2	3	4		$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$		$f=3$	
$s=0$			2	Quintet $i_r=\frac{4}{2}$			$\frac{5}{2}$	Sextet $i_r=\frac{5}{2}$			$s=0$		
$p=1$		1	2	3			$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$			$p=1$	
$d=2$	0	1	2	3	4		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$d=2$	
$f=3$		1	2	3	4	5	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$f=3$	

Taking the case of two valence electrons, if electron (1) gives a term $(n^r_{kj})_1$, electron (2) gives a term $(n^r_{kj})_2 \dots$ the resultant term is N^R_{Kj}

$$\text{where } i_R = \text{vector sum of } (i_r)_1, (i_r)_2$$

$$i_K = \text{,, ,, ,, } (i_k)_1, (i_k)_2$$

The rule for addition of i_j is more complicated and will be taken later.

Thus taking $M_1 N_1$ -state, we have

$$\text{for } M_1, i_r = \frac{1}{2}, i_k = 0$$

$$N_1, i_r = \frac{1}{2}, i_k = 0$$

$$i_R = \left| \frac{1}{2} + \frac{1}{2} \right| = 0 \quad \text{and} \quad \frac{2}{2}$$

$$i_K = |0 + 0| = 0$$

The resultant terms are

$$(1) \quad i_R=0, \quad i_K=0, \quad \text{i.e. } {}^1S_0$$

$$(2) \quad i_R=\frac{2}{2}, \quad i_K=0, \quad \text{i.e. } {}^3S_1$$

Taking, $M_1 N_2$ state, we have

$$\text{for } M_1, i_r = \frac{1}{2}, i_k = 0 \left\{ \begin{array}{l} i_R=0, \text{ or } \frac{2}{2} \\ i_K=1 \end{array} \right.$$

$$N_2, i_r = \frac{2}{2}, i_k = \frac{1}{2} \left\{ \begin{array}{l} i_R=1 \end{array} \right.$$

The resultant terms are 1P and 3P .

Now we see that the origin of all the higher terms in Mg except in the normal state where instead of two terms ${}^1S_0, {}^3S_1$, only 1S_0 appears, 3S_1 is definitely absent. In $M_1 M_1$, both the electrons are in absolutely equivalent orbits. Hence there must be some law of exclusion forbidding the appearance of certain terms in equivalent orbits.

Rules for j -summation.—To understand this phenomena, i.e. non-appearance of the term when equivalent orbits are synthesised we take the rule for j -summation.

Now j denotes the total quantum number, and we know from Zeeman effect data that we have to introduce a magnetic quantum number m , which is the quantum-projection of j on an axis fixed in space

Hence

$$m = \pm(j, j-1, j-2 \dots) \text{ up to } 0, \text{ or } \pm 1$$

$$i_m = \pm(i_j, i_{j-1} \dots)$$

$$\text{Thus for } {}^2S_1\text{-term, } i_j = \frac{1}{2}, i_m = \pm \frac{1}{2}.$$

The two 2S_1 -electrons (or their orbits) may be so oriented that their i_m -values = $\frac{1}{2}$ or $-\frac{1}{2}$. According to Pauli, if they are in the same level the magnetic quantum number of no two electrons should be the same. Thus

$$\text{if for electron (1) } i_m = +\frac{1}{2}$$

$$\text{for electron (2) } i_m = -\frac{1}{2}$$

and resultant $i_M=0$.

Thus the shell will possess no resultant magnetic moment. This explains why in equivalent orbits there should be a normal 1S_0 -term only and no 3S_1 -term.

But when one electron is fixed in a 2S_1 -orbit the second shifts to a higher 2S_1 ($n=2$), we have

$$\begin{array}{r} (i_m)_1 = \frac{1}{2} \dots - \frac{1}{2} \\ (i_m)_2 = \frac{1}{2} \dots - \frac{1}{2} \\ \hline i_M = 1 \quad 0 \quad -1 \end{array}$$

The last combination corresponds to a 3S_1 -term. Pauli's Principle of Exclusion also explains why there should be no more than six electrons to fill up completely the L_2 -shell (shells in which all electrons have doublet P -characteristics). For here the full number of magnetic quantum numbers is six, viz.

$$\left. \begin{array}{l} \text{for } {}^2P_{\frac{1}{2}}, \quad i_m = \frac{1}{2} \quad -\frac{1}{2} \\ {}^2P_{\frac{3}{2}}, \quad i_m = \frac{3}{2}, \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{3}{2} \end{array} \right\}$$

If we take the L_2 -level, the maximum number of electrons is the number corresponding to all the possible different values of i_m viz. 6. Hence 6-electrons are required to fill up any P_2 -level completely. When this occurs, as in Ne, the resultant $i_r=0$, $i_k=0$, $i_m=0$, hence it gives an 1S_0 -term, the atom is absolutely neutral.

A similar consideration applied to the d -level shows that the maximum number of electrons required to fill up this level is 10, for an f -level it is 14.

The Periodic Classification.—The periodic classification is now easily explained. Let us take the two groups of elements and consider the constitution of external levels lying beyond closed groups.

Outer shell				Outer shell			
3. Li	$2K_1$	L_1	s^1	11. Na	$2K_1$	$8L$	$M_1 s^1$
4. Be	"	$2L_1$	s^2	12. Mg	"	$2M_1$	s^2
5. B	"	$2L_1$	$L_2 s^2 p^1$	13. Al	"	$2M_1$	$M_2 s^2 p^1$
6. C	"	$2L_1$	$2L_2 s^2 p^2$	14. Si	"	$2M_1$	$2M_2 s^2 p^2$
7. N	"	"	$3L_2 s^2 p^3$	15. P	"	$3M_2$	$s^2 p^3$
8. O	"	"	$4L_2 s^2 p^4$	16. Se	"	$4M_2$	$s^2 p^4$
9. Fl	"	"	$5L_2 s^2 p^5$	17. Cl	"	$5M_2$	$s^2 p^5$
10. Ne	"	"	$6L_2 s^2 p^6$	18. A	"	$6M_2$	$s^2 p^6$

The outer constitution is essential for chemical constitution. Both Li and Na contain only one s -electron, hence they are monovalent. Be and Mg each contain 2 s -electrons, they are divalent. B and Al each contain 3 electrons, two s -electrons and one p -electron. There is no great energy difference between s - and p -electrons and all three can contribute to chemical valency (more in detail later). Similar considerations apply to the other remaining elements.

The optical spectra of corresponding elements are essentially similar. The spectra of one valence and two valence elements have been already considered. From B to Ne or from Al to A, the outer shell consists of 2 s -electrons and 1, 2, ... up to 6 p -electrons. The normal optical levels are given by vectorial addition of the quantum characteristics of all these electrons. The 2 s -electrons, forming a closed shell contribute nothing. The terms arising out of the synthesis of the orbits of varying number of p -electrons are shown in Table 2. They are calculated (16) by applying Pauli's principle that in equivalent orbits, no two electrons will have the same i_m -value. The calculation of terms is extremely complicated and has not been reproduced.

TABLE 2

Number of p -Electrons			
1	${}^2P_{1,2}$		
2	${}^3P_{0,1,2}$	${}^1\bar{D}_2$	${}^1\bar{S}_0$
3	4S_3	${}^1\bar{D}_{2,3}$	${}^2\bar{P}_{1,2}$
4	${}^3P_{0,1,2}$	${}^1\bar{D}_2$	${}^1\bar{S}_0$
5	${}^2P_{1,2}$		
6	1S_0		

Dashed and Undashed Terms.—Some explanatory remarks may be made here regarding the dashing of terms. The rule is that if a number of terms arise from a particular combination of electron, they must have all the same combinatory properties, provided the selection rule for the inner quantum number j is verified. Supposing now that from a particular combination say p^2 above, S , P , and D terms arise, they must have all the same combinatory powers, and cannot combine amongst themselves. But if they are all denoted as merely $S_1 P_1 D_1$ then according to the usual convention, the P can combine with S or D -terms. To express that this is not possible, we provide S and D with a bar (dashing). Thus P and $\bar{D}$ have the same combinatory powers, and cannot combine amongst themselves, except under exceptional circumstances. We can express the same fact by dashing P , and keeping S and D undashed. It is purely a matter of convention in which we have to be guided by our previous knowledge of the spectrum of the element.

The next elements are Outermost shell

19. K	$2K \cdot 8L \cdot 8M$	$N_1: N_1$	..	s^1	alkali-monovalent
20. Ca	$2K \cdot 8L \cdot 8M$	$2N_1: 2N_1$	..	s^2	alkaline-divalent earth

The constitution of the outermost level of K, and Ca are exactly similar to those of Na and Mg respectively. The chemical properties are therefore similar. But a new feature is now present. We have now an M_3 -level next to the M_2 -level horizontally and lying diagonally opposite N_1 . Such a feature was not present in the elements treated

Now there is again an N_3 -level with larger negative energy value than O_1 , hence in element 39, the electron goes by preference to N_3 . We thus get the formation of the next transitional group.

TRANSITIONAL GROUP II (13)

39. Y		$2N_3O_1$	$N_3.2O_1$	$d^3 s_1, ds^3$
40. Zr		$3N_3.O_1$	$2N_3.2O_1$	$d^3 s_1, d^3 s^2$
41. Nb		$4N_3O_1$	$3N_3.2O_1$	$d^4 s^1, d^3 s^2$
42. Mo		$5N_3.O_1$	$4N_3.2O_1$	$d^5 s^1, d^4 s^2$
43. Ma.				
44. Ru	...	$8N_3, 7N_3O_1, 6M_3.2O_1$		$d^8, d^7 s^1, d^6 s^2$
45. Rh		$8N_3O_1$		$d^9, d^8 s^1, d^7 s^2$
46. Pd		$10N_3, 9N_3O_1, 8N_3.3O_1$		$...d^{10}, d^9 s^1, d^8 s^2$

From 47 to 54, we have now another regular group formed. We have

47. Ag		$10N_3.O_1$	s^1
48. Cd		$10N_3.2O_1$	s^2
49. In		$10N_3.2O_1.O_2$	$s^2 p^1$
50. Sn		$2O_2$	$s_2 p^2$
51. Sb		$3O_2$	$s_2 p^3$
52. Te		$4O_2$	$s_2 p^4$
53. I		$5O_2$	$s_2 p^5$
54. Xe		$6O_2$	$s_2 p^6$

55 and 56 again give us an alkali and alkaline earth. Thus

55. Cs		$6O_2.P_1$	s^1
56. Ba		$6O_2.2P_1$	s^2

With the next element, a new feature reveals itself. We find from the table of energy values for different levels that N_4 has larger negative energy value than O_3 . Hence in the next elements, the N_4 -level will be filled up. This requires 14 electrons and we have accordingly a group of 14 elements from 57 La to 70 Yb with entirely new properties viz., the rare-earths. The composition of their outer shells is yet unknown, as their spectra have not yet been fully investigated.

In the formation of the next group of elements, the electrons fill the level O and thus form the transitional group III. The electronic structure of the outer levels will be similar to those of the other transitional groups or may differ from them in non-essential points.

The outer shell of Hf has the same electronic structure as Ti and Zr.

This was first pointed out by Bohr, whereas according to the older view element 72 was regarded as a rare earth and trivalent. As is well known Hevesy and Coster acting under the guidance of Bohr, discovered Hf in association with Zirconium minerals.

After the levels N_4 and O_3 are filled, the next electrons

will continue to fill P_1, P_2 ; we thus get the following regular group ending in an inert gas.

79. Au		$14N_4.10O_3$	P_1	s^1
80. Hg			$2P_1$	s^2
81. Tl			$2P_1.P_2$	$s^2 p^1$
82. Pb			$2P_2$	$s^2 p^2$
83. Bi			$3P_2$	$s^2 p^3$
84.				
85.				
86. Rad Em.				

In the next elements, Q is being filled up. We get

87. Eka Cs		Q_1	Alkaline.
88. Ra		$2Q_1$	Alkaline Earth.

Elements 98 ... 102 will form Rare earth II.

102 ... 112 Transitional group IV.

112 ... 118

118 being a rare earth.

But as is well-known, our knowledge at present ends with 92 (Ur).

The structure diagram thus probably affords the most satisfactory explanation of the origin of periodic properties of Atoms. It explains not only the general features, but also even the minute details.

Summary of the Periodic Classification.—Chart 1 thus graphically visualizes the formation of different groups in which the elements can be subdivided according to the structure of their outer shells, on which the chemical properties are assumed to depend. We have

a) H and He which quite stand apart. Spectroscopically they form the same group as the elements in which an s -level is being filled up, namely the short group of two consisting of an alkali and an alkaline earth. These are

1. 19 K and 20 Ca
2. 37 Rb ... 38 Sr
3. 55 Cs ... 56 Ba
4. 87 ... 88 Ra

But owing to the very high ionisation potential, He is inert. Hydrogen quite stands apart. The spectra of corresponding elements are perfectly analogous.

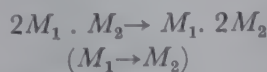
In these short groups, the s -levels are being filled up.

b) Regular groups, 5 in all, consisting of

1. 3 Li to 10 Ne
2. 11 Na .. 18 A
3. 29 Cu .. 36 Kr
4. 47 Ag .. 54 Xe
5. 79 Au .. 86 Nt

Here the s and p -levels lying in the same horizontal line (with the same value of total quantum number) is being filled up. The valency varies from 1 to 7 and then falls to zero.

It might be thought that in B and Al, since the s -level is completely filled up, the p -electron would be the only one which can be easily detached off. But it is found that in these elements, and probably in the higher elements of these groups, the s -electron can easily pass to the p -stage i.e. we have lines corresponding to the transition (taking Al):



Again $M_1 \cdot 2M_2 \rightarrow 3M_2$.

Hence all the three electrons can contribute to valency. Similar inner transitions have been observed in C, and are probably true of all elements up to the combination $(2X_1 5X_2)$.

c) Transitional groups— three in number consisting of

1. 21 Sc to 28 Ni
2. 39 Y to 46 Pd
3. 71 Lu to 78 Pt

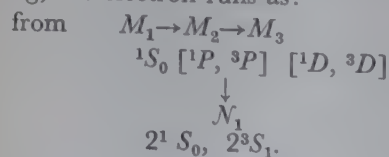
and a fractional group 89 Ac- 92 Ur and other undiscovered elements.

In these groups, the d -level is being filled up, the general composition of outer levels is $d^x s^3$, $d^{x+1} s^1$, x varying from 1 to 8.

d) The rare earths group consisting of 14 elements, 57 La to 70 Yb, in which the N_4 , or the f -level is being filled up. The outer composition is still optically unknown. The composition may be $f^x d^y s^{1/2}$ where $x+y$ vary from 1 to 14, and f refers to N_4 , d refers to O_3 .

General Treatment of the Spectra of Elements. Two Valence Elements.

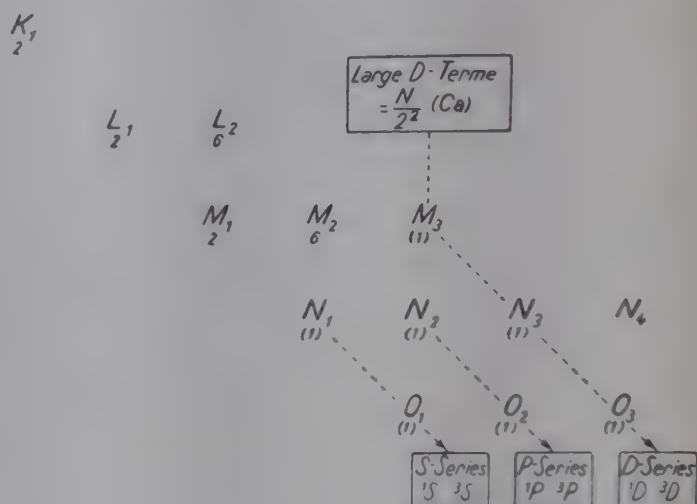
We have previously remarked that when we compare the structure diagrams of Mg and Ca, a difference is at once observed. We shall treat this phenomena more in detail. In Mg, the electron runs as:



$2^1 P_1$ is approximately $\frac{R}{2^2}$, the first $1D = \frac{R}{3^2}$. But let us take (vide page. 379).

In Ca, there is an empty M_3 -level, lying diagonally opposite N_1 , and hence equal in energy value to N_1 . Actually the first D -term is found to be approximately $R/2^2$. These large D -levels form the characteristic feature of the spectra of Ca and also of Sr and Ba, while Cd and Hg are perfectly analogous to Mg. These levels are really metastable compared to the normal levels. According to Bohr's enumeration, the total quantum number corresponding to this D -term viz. 3, is less than even that of the first s -term viz. 4.

STRUCTURE DIAGRAM OF Ca



Anomalous Terms (19).—The influence of these metastable levels is clearly seen in the «anomalous terms» obtained in the spectra of Ca, Sr and Ba. They were first thoroughly investigated by Saunders and Russell. To obtain them, we have to keep the fixed electron at M_3 (for Ca), and allow the running electron to pass through the higher levels. The terms expected and observed are shown in Table 4.

There are anomalous terms in the spectra of Mg, Zn and Hg, but they are quite of a different nature. They are obtained when the fixed electron is kept at M_2 , and the running electron runs through the higher levels.

Rydberg sequence in Anomalous Terms—Negative Terms.—Even in anomalous terms, we get Rydberg sequence, when we collect terms obtained by displacing the electron diagonally. For example, take the $M_3 X_3$ -combination in Ca, and compare the values of the successive p -terms arising from this combination with the values of the p -terms arising from the normal D -sequence of $N_1 X_3$ combination. They are shown graphically below:

$M_3 M_3$	$M_3 N_3$	$M_3 O_3$	$M_3 P_3$	$M_3 Q_3$
$1^1 \bar{P}, 1^3 \bar{P}$	$2^1 \bar{P}, 2^3 \bar{P}$	$3^1 \bar{P}, 3^3 \bar{P}$	$4^1 \bar{P}, 4^3 \bar{P}$	$5^1 \bar{P}, 5^3 \bar{P}$
$N_1 M_3$	$N_1 N_3$	$N_1 O_3$	$N_1 P_3$	$N_1 Q_3$
$1^1 D, 1^3 D$	$2^1 D, 2^3 D$	$3^1 D, 3^3 D$	$4^1 D, 4^3 D$	$5^1 D, 5^3 D$

Of the set of terms from $M_3 X_3$, we have taken only the $\bar{P}$ -set. Compare the values of each corresponding pair in each vertical column:

$$\begin{aligned} \text{Now } M_3 Q_3 \rightarrow N_1 Q_3 &= (M_3 \rightarrow N_1) Q_3 \\ &= (M_3 \rightarrow V_1) \text{ of Ca}^+, Q_3 \text{ being far off, is neglected} \\ &= {}^3 D - {}^3 S \text{ of Ca}^+ \\ &= -13711 \end{aligned}$$

TABLE 4

State	Present notation	Russell & Saunders' notation	Term values		
			Ca.	Sr.	Ba.
(a) M_3M_3	$^3\bar{F}_{4,3,2}$	..	..	..	19077.9 19510.1 19990.3
	$^3\bar{P}_{2,1,0}$	p'	10753.0 10839.8 10887.1	86.8 47.3	18110.5 18549.3 18820.3
	1S_0	X	8584.9	8964.9	9929.0
	1D_2				
	1G_4				
(b) M_3N_3	$^3F_{4,3,2}$	f''	13407.6 13485.9 13573.9	78.3 88.0	18372.6 19082.1 19964.8
	$^3D_{3,2,1}$	d'	11045.3 11085.3 11112.0	40.0 26.7	17049.8 17498.1 17837.6
	$^3P_{2,1,0}$	p''	9964.3 9969.1 9971.0	4.8 1.9	16073.1 16325.5 16387.8
	1F_3	Y	8767.0	9836.1	15213.4
	1D_2				
	1P_1				
	$^2D_{3,2,1}$	..	..	..	13475.2
	2D_2				
	2D_1				
	2D_0				
(c) M_3O_1	$^2D_{3,2,1}$	..	..	..	4526

i.e. the higher P-terms will be less than the corresponding P-terms by 13711. The actual values of the sequence are shown below:

	$1^3\bar{P}$	$2^3\bar{P}$	$3^3\bar{P}$	$4^3\bar{P}$	$5^3\bar{P}$
$^3D-(^3S-^2D)$	10840	767	-4983	-8313	-10063
$^3D-(^1S-^2D)$	15306	-2097	-7090	-9359	-10649
	7106				

Thus the higher terms of a Rydberg sequence arising from a metastable fixed level become negative, as was first shown by Saunders and Russell.

Ionised Elements with two Valence Electrons.—The anomalous terms become more prominent as we pass on from Ca to Ba. This is because the unbalanced electrical field of the Barium nucleus is larger than that of the Ca-nucleus.

When we take the elements Sc^+ , Y^+ , and L^+ which have got the same number of electrons as Ca, Sr and Ba respectively, we find actually that the d -level is much more stable than the s -level e.g. in Sc^+ , the M_3 -level is much more stable than the N_1 -level. So in the spectrum of Sc^+ , terms obtained with the fixed electron at M_3 are much larger than that the terms obtained with the fixed electron at N_1 —in other words, though Sc^+ has a structure similar to that of Ca, the spectrum is just reversed,—the anomalous terms become normal, and the normal terms become

anomalous. Thus the displacement rule of Sommerfeld and Kossel is not strictly true or holds only in a qualified sense.

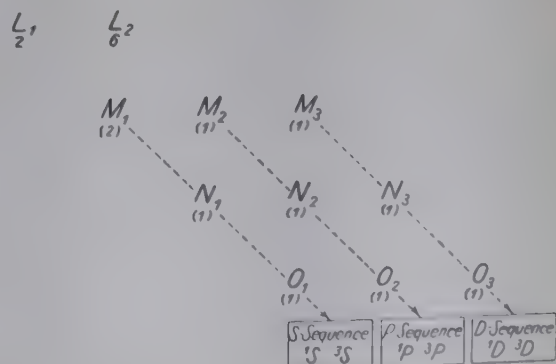
Spectra of Elements of Group III

B, Al, Ga, In and Tl.

Taking Al, we find that the structure diagram is:

STRUCTURE DIAGRAM OF Al

K_1



The term values and their origin are shown below.

Combination	Terms	Term-values	Remarks
$b_0) M^2$	${}^2P_{1,2}$ = and sequence	$\left. \begin{array}{l} 48168.87 \\ 280.88 \\ 15316 \\ 331 \end{array} \right\}$ etc.	Normal terms
$c_1) M_3$	${}^2D_{3,3}$ =	$\left. \begin{array}{l} 15845.5 \\ 844.2 \end{array} \right\}$ etc.	$b_0 {}^2P-c_1 {}^2D$ roughly follows the irregular doublet law, because the total quantum number is the same.
$a_1) N_1$	2S_1 =	$\left. \begin{array}{l} 22933.3 \\ 10592.6 \end{array} \right\}$	$b_0 {}^2P-a_1 {}^2S_1$ does not follow the irregular doublet law. Total quantum number different.
$a_1) M_1.2M_3$	$4\bar{P}$ ${}^2\bar{P}_{1,3}$ ${}^2D_{3,3}$ 2S_1	$\left. \begin{array}{l} ? \\ -8361 \\ -8249 \\ ? \\ ? \end{array} \right\}$	Combination $P\bar{P}$ corresponding to the inner transition $2M_1M_2 \rightarrow M_1.2M_3$ has been discovered by Millikan and Bowen in case of Al, and by Kichlu in case of Si^+ . So this transition is possible in all three valence spectra.

The spectra of three-valence elements including B, Al, Ga, In, Tl, are comparatively simple. If we compare the spectra of Al, Si^+ , P^{++} , etc. . . which all ought to be similar, we find that the ${}^2P-{}^2D$ lines follow the irregular doublet law roughly, ${}^2P-{}^2S$ lines not at all (Table 5). The inner transition $2M_1M_2 \rightarrow M_1.2M_3$ is very interesting. Here also the total quantum number remains unchanged, and the irregular doublet law is better followed than in the case of the ${}^2P-{}^2D$ lines, (Table 6), taken from a paper by Bowen and Millikan illustrates the point.

TABLE 5

	Al	Si^+	P^{++}	S^{+++}	Cl^{+4}
${}^2P-{}^2D$	32325 (46371)	79056 (37265)	116321 (34868)	151189 (33200)	184390
${}^2P_1-{}^2S$	25348 (40147)	65495			

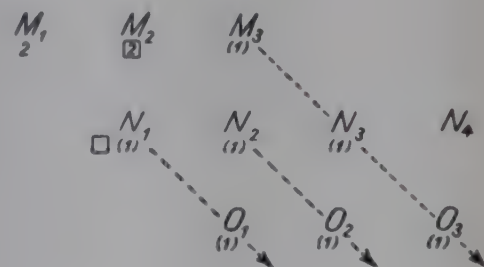
TABLE 6

$2M_1-M_3$ $M_1.2M_3$	Al	Si^+	P^{++}	S^{+++}	Cl^{+4}
${}^2P-{}^2\bar{P}$	56615 (27202)	83717 (25134)	108850 (24441)	133292 (24111)	157403
${}^2P-{}^2D$		55305			
${}^2P-{}^2S$		63613			
${}^2P-{}^4\bar{P}$					

Literature—MILLIKAN & BOWEN, P. R., vol. 26, p. 160. P. K. KICHLU, I. O. S. A. vol. 14, p. 455.

Group IV - Four Valence Elements

STRUCTURE DIAGRAM OF Si .

 $K,$
 $2,$
 $L,$
 $2,$


The expected terms and their values and combinations are shown below.

THE SPECTRUM OF Si

$b_0) {}^2M_2$	3P_0 64275	3P_1 64198	3P_2 (6076) 64051	1D_2 (9095) 57975	1S_0 48880
$a_1) M_2N_1$					
24592... ${}^3\bar{P}_0$	—	(8) 39606	—	—	—
24515... ${}^3\bar{P}_1$	(7) 39760	(7) 39683	(9) 39537	(5) 33461	(5) 24366
24320... ${}^3\bar{P}_2$	—	(9) 39878	(10) 39732	—	—
23823... ${}^1\bar{P}_1$	40991	40914	40768	(10) 34693	(9) 25598

$c_1) M_2 M_3$						
	$^3\bar{F}_2$		?	?	?	
	$\bar{F}_3$		?	?	?	
	$\bar{F}_4$					
18999...	3D_1	45276	45199	45052	(35957)	(26862)
18982...	D_2		45216	45069	(35974)	
18954...	D_3			45098		
13672...	3P_0		50526			
13707...	P_1	50568	50491	50344	(44268)	(35173)
13774...	P_2		50424	50277		
	$^1\bar{F}_3$			?	?	
	1D_2		?	?	?	
	$^1\bar{F}_1$	?	?	?	(41053)	

$\alpha_1) M_1 3M_2$						
	4S_2					
	3S_1					
	3P_0					
	P_1					
	P_2		Still Unknown			
	1P_1					
	3D_1					
	D_2					
	D_3					
	1D_2					

As regards the spectrum of C, it is not yet completely done. The spectra of Ge, Sn and Pb are exactly alike that of Si, only the intercombinations are stronger, in conformity with the general rule. The inner transition groups

$$2M_1 2M_2 \rightarrow M_1 3M_2$$

$$M_1 \rightarrow M_2$$

obey the irregular doublet law, as pointed out by Bowen and Millikan in the case of C, N⁺, O⁺⁺, Fl⁺⁺⁺ (Table 7).

In the case of Pb, owing to its large atomic weight, the $\Delta v^2 P_1 - 2P_2$ of Pb⁺ is abnormally large about 19010. Hence only terms proceeding from 2P_1 of Pb⁺ are developed completely. For details, see Sur, (Phil. Mag.), Vol. 2, p. 633.

TABLE 7

	$b_0^3P - \alpha_1^3S$	$b_0^3P - \alpha_1^3P$	$b_0^3P - \alpha_1^3D$
C		75211	64046
		33875	28060
N ⁺	154996	109087	92106
	41785	32987	27612
O ⁺⁺	196781	142075	119719
	40918	32551	27514
Fl ⁺⁺⁺	237699	174627	147234

Elements of Group IV

C, Si, Ge, Sn, Pb.

In elements of this group, the normal electron configuration is $2X$ i.e. there are two electrons with p -characteristics. They will give us resultant terms

$$\begin{array}{ccc} ^3D & ^3P & ^3S \\ ^1D & ^1P & ^1S \end{array}$$

for $\begin{array}{ccc} (i_k)_1=1, & (i_k)_2=1 & I_k=2, 1, 0 \\ (i_r)_1=\frac{1}{2}, & (i_r)_2=\frac{1}{2} & I_r=0, \frac{2}{2} \end{array}$

but of these terms, a few are forbidden by Pauli's exclusion principle, as long as electrons are both in M -positions. It is found that the admissible terms are $^3P_{0,1,2}$, $^1\bar{D}_2$, $^1\bar{S}_0$. The D and S -terms must be barred because they have the same combinatory properties as the P 's.

Literature—MACLENNAN, P. R. S. (Canada), vol. 20 (1926), for Ge, C, Si, Sn, Pb; N. K. Sur, Zs. f. Physik, Bd. 41, p. 791, for Sn; for Si, Fowler, Phil. Trans., 225, p. 1. For Pb. Grotrian, Zs. f. Physik, Bd. 34, p. 374; Sur, Phil. Mag. vol. 2, p. 633. BOWEN and MILLIKAN, P. R. 29, p. 240.

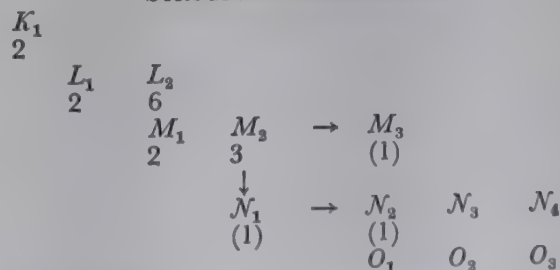
Elements of Group V

N, P, As, Sb, Bi.

According to Hund's theory all these elements have $3P$ -electrons in the normal state.

The typical structure diagram is given by that of Phosphorus:

STRUCTURE DIAGRAM OF P



Combination

$$\begin{array}{l} (a) 3M_2 \\ (b) 2M_2 N_1 \\ (c) 2M_2 N_3 \\ (d) 2M_2 N_2 \end{array} \quad \begin{array}{l} ^4S_2 \quad ^3D_{2,3} \quad ^3\bar{P}_{1,2} \\ ^4P, \quad ^2P \quad ^2\bar{S} \quad ^2P \end{array}$$

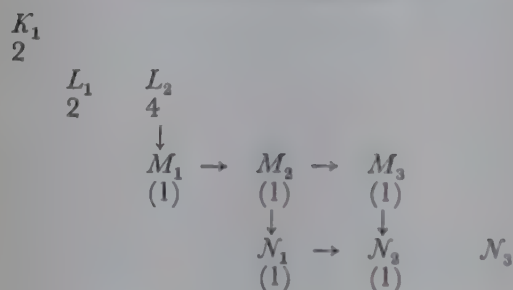
The spectra of none of elements have yet been completely cleared up, but the spectrum of O^+ will have similar constitution, and this has been analysed partially by A. Fowler. R. H. Fowler and Hartree have shown that A. Fowler's analysis is completely in accord with Hund's theory. Recently Bowen and Millikan have identified the fundamental 4S_2 -level of O^+ , and another two fundamental levels, but it is difficult to say if this is 3P or 2D .

Elements of Group VI

O, S, Se, Te, Po.

These elements have 4- P -electrons in the outer shell, and to get a picture of the spectrum, we can take the structure diagram of O.

STRUCTURE DIAGRAM OF O.



Combination	Terms expected	Terms observed
a) $4L$	$^3P \ ^1\bar{D}_2 \ ^1\bar{S}_3$	
b) $3L_2 \ M_1$	$^3S, \ ^3S; \ ^3\bar{P} \ ^1\bar{P}, \ ^3D \ ^1D$	
c) $3L_2 \ M_2$	$^3P, \ ^3P$	
d) $3L_2 \ N_1$	$^3S, \ ^3S;$	
e) $3L_2 \ M_3$	$^3D, \ ^3D$	

The normal terms 3P have been obtained by Hopfield in the case of O and S. The lines of O and Se in the visible range have been partially analysed by Fowler, and they arise from the level b) Rydberg sequences corresponding to transitions $3M_2X_1$ ($X_1=N_1, O_1, P_1, \dots$) have been obtained.

Elements of Group VII (Halogens)

Seven Electron Elements

STRUCTURE DIAGRAM

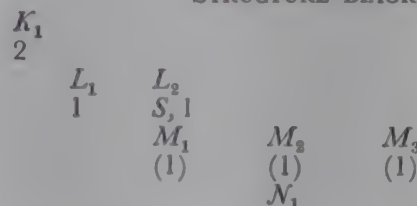


TABLE 8.

$4L_2M_1$	$4\bar{P}_1$ (160)	$4\bar{P}_2$ (274.5)	$4\bar{P}_3$	1P_1 (325)	3P_1	3D_2	3D_3	3S_1	
$\left\{ \begin{array}{l} 5L^2 \\ ^3P_1 \\ 409 \\ ^3P_2 \end{array} \right.$				104654	104331	123928	(?)		Fundamental terms
				105063	104736		123518		
$4L_2M_2$									
$4\bar{D}_1$	(20) 14468	(3) 14712							
83 $\bar{D}_2$	(18) 14552	(18) 14628	(1) 14903						
177 $\bar{D}_3$		(30) 14484	(20) 14758						
144 $\bar{D}_4$			(40) 14582						
$4P_1$	(13302)	(12) 13462							
102 P_2	(5) 13201	(5) 13360	(18) 13634						
212 P_3		(5) 12238	(20) 13512						
$4S_2$	(23) 15588	(28) 15748	(30) 16022						
2D_2	14782	14942	15217						
D_3									
2P_1	15192	15032		(5) 14025	(4) 14351				
145 P_3				(15) 13881	(50) 14206				
2S_1				(3) 15581	(1) 15727 (?)				

The spectra of Fl has been analysed by Dingle, de Bruin, and Bowen and of Ne⁺ which is similar to that of Fl) by P. K. Kichlu, and Bruin. The combinations in the case of Fl are shown in Table 8, intercombination have not yet been traced.

Elements of Group VIII (Inert Gases)

Eight Electron Elements (s^2p^6)

STRUCTURE DIAGRAM OF NEON

$$\begin{array}{ccccccc}
K_1 & & & & & & \\
2 & & & & & & \\
L_1 & L_2 & & & & & \\
2 & 5,1 & & & & & \\
& M_1 & M_2 & M_3 & & & \\
& (1) & (1) & (1) & & & \\
& & N_1 & N_2 & N_3 & N_4 & \\
& & (1) & (1) & (1) & (1) & \\
& & & O_1 & O_2 & O_3 & O_4 \\
& & & (1) & (1) & (1) & (1)
\end{array}$$

The spectrum of Neon was first analysed by Paschen and Meissner, and its interpretation in terms of the quantum mechanics has been successively given by Goudsmit, Hund, and Saha. The expected terms and combinations, with their values are shown below. The spectrum of Argon has recently been analysed by Meissner, and it is quite in agreement with Hund's theory.

The combination $5L_2 M_2 - 5L_2 M_3$ has also been disco-
 $(M_2 \rightarrow M_3)$

vered, as well as the higher Rydberg sequence of all the previous sets. There is a certain amount of uncertainty in the designation of the terms, when the inner quantum number proves to be the same e.g. terms designated 3P_1 and $^1\bar{P}_1$ may be interchanged. The spectrum of Neon also deviates from the general rule that in elements of small atomic weight, intercombinations are either absent, or very faint. The intercombinations in Ne are seen to be quite strong. Some of the sequences follow the Rydberg law only if 782 be added to them. They are the terms arising from the 2P_2 state of Ne^+ .

Spectra of Elements belonging to the Transitional Groups.

As has been remarked before, the outer shell of the transitional group of elements in the normal state has the constitution $d^{x_s 1}, d^{x-1} s^2$. The normal terms can easily be calculated making use of Chart 1), and the other rules of term synthesis. The higher terms are obtained by allowing one

EXPECTED TERMS AND COMBINATIONS OF THE SPECTRUM OF NEON

$5L_2M_1$ P^3S^1	3P_0 39111	3P_1 39470	3P_2 39888	1P_1 38041	Remarks
b_0) $6L_2^1S_0$ 173970	—	(743.5) 134500	—	(735.7) 135929	} Normal state
b_1) $5L_2M_1$	—	—	—	—	
3D_1 (23808)	(6) 15303	(12) 15662	(11) 16080	(9) 14233	
3D_2 (23614)	— —	(8) 15798	(12) 16220	(10) 14427	
3D_3 (24272)	—	—	(20) 15615	—	
3P_0 (23012)	—	(10) 16458	—	(7) 15029	
P_1 (22891)	(12) 16220	(10) 16579	(20) 16997	(15) 15150	
P_2 (23071)	— —	(8) 16399	(8) 16817	(9) 14970	
3S_1 (25672)	(8) 13439	(10) 13798	(10) 14216	(8) 12369	
1D_2 (24105)	—	(15) 15364	(10) 15782	(10) 13935	
1P_1 (23157)	(15) 15954	(6) 16313	(12) 16730	(2) 14883	
1S_0 (20959)	—	(50) 18511	—	(50) 17082	

outer electron, generally the *s*-electron, to run through the higher levels, as shown in the following diagram:

$$\begin{array}{ccccccc}
K_1 & & & & & & \\
2 & & & & & & \\
L_1 & L_2 & & & & & \\
2 & 6 & & & & & \\
M_1 & M_2 & M_3 & & & & \\
2 & 6 & x & & & & \\
N_1 & N_2 & N_3 & N_4 & & & \\
y & (1) & (1) & & & & \\
O_1 & O_2 & O_3 & & & & \\
(1) & (1) & (1) & & & &
\end{array}$$

The term-systems are extremely complicated, but are in every case so far investigated, in complete agreement with Hund's theory. Usually only normal terms and the terms next to them have been obtained. Except in the case of Mn, Cr, and Co, Rydberg sequence has not yet been established in an unambiguous manner.

There are again slight differences in the composition of the outer shell in Group 1) and Group 2) of Transitional Elements. In group 1, the structure is generally

$$(x-1) \begin{matrix} x M_3 N_1 \dots d^x s^1 \\ M_3 2N_1 \dots d^{x-1} s^2 \end{matrix}$$

In group 2, for a corresponding element, the structure is

$$(x+1) \begin{matrix} M_3 \dots d^{x+1} \\ x M_3 N_1 \dots d^x s^1 \end{matrix}$$

For example, let us compare the structure of Ni and Pd.

$$\left. \begin{matrix} Ni \dots 8M_3 \cdot 2N_1 \dots d^8 s^1 \\ 9M_3 \cdot N_1 \dots d^9 s^1 \end{matrix} \right\} \quad \left. \begin{matrix} Pd \dots 9N_3 \cdot O_1 \dots d^9 s^1 \\ 10N_3 \dots d^{10} \end{matrix} \right\}$$

Ionisation Potential of Elements.—Curve A) shows graphically the ionisation potential of elements from H to Ga. It will be seen that there are well-marked periods of 2, 6, and 10. Whenever a shell is completed the ionisation potential reaches a maximum value. For incomplete groups, the ionisation potential gradually increases with the number of electrons in the group, e.g. compare the part of the curve from Al to A, or from Sc to Ni.

Why the two apparently distinct sub-levels L_{21}, L_{22} have been combined in one level.

In the atomic diagram of Stoner and Main Smith, the L_2 level was split up into two sublevels L_{21}, L_{22} containing 2 and 4 electrons respectively. Similarly the M_3 -level was split up into M_{32}, M_{33} , containing 4 and 6 electrons respectively. This splitting is found unnecessary. No use has been made of it in the calculation of optical terms. If such a splitting existed, either the M_{32} or M_{33} level should first be filled up before the electron goes to the other sublevel.

In this case, the part of the ionisation potential curve, from Al to A, or Sc to Ni, would not be continuous but would show a maximum at Si, and Cr corresponding to the filling up of the L_{21} and M_{22} levels respectively. Since there is no evidence of such maxima, there is no statical splitting of these levels into two sublevels.

Characteristic X-Ray Spectra of Elements. (20)—It is sometimes thought that for the explanation of X-ray spectra of elements, the subdivision of the p or d -levels into two distinct sublevels is necessary. But as has been shown by Dr. B. B. Ray and the author, X-ray spectra can be explained on the same principles as optical spectra, e.g. let us take the K -series of any elements. We take the structure diagram, and suppose that either by electron bombardment or otherwise, one electron has been removed altogether from the K -level. Then the state is unstable, one electron will now fall from any p -level ($L_2, M_2, N_2 \dots$) to the K -level. The process can be written as follows:

$$K_1 \cdot 6L_2 \rightarrow 2K_1 \cdot 5L_2$$

$$(L_2 \rightarrow K_1) \dots \text{gives us } K\alpha, K\alpha'$$

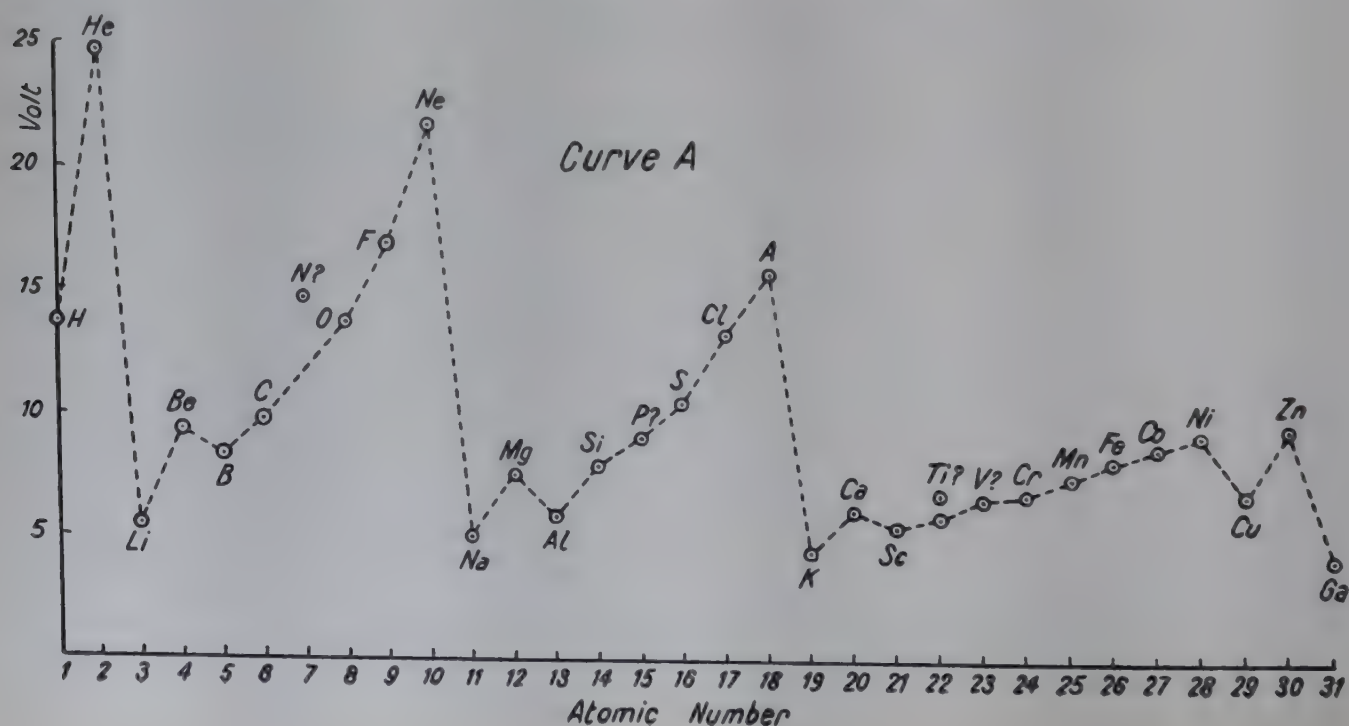
$$K_1 \cdot 6M_2 \rightarrow 2K_1 \cdot 5M_2$$

$$(M_2 \rightarrow K_1) \dots \dots \dots K\beta, K\beta'$$

Now $K_1 \cdot 6L_2$ gives us a 2S_1 -orbit.

$2K_1 \cdot 5L_2$ gives us a ${}^2P_{1,2}$ -orbit.

(K_1 gives 2S_1 , $6L_2$ gives 1S_0 ; the resulting orbit is 2S_1 . For the second state 2K_1 gives 1S_0 , 6L_2 gives ${}^2P_{1,2}$ as in the halogens; the resulting orbit is ${}^2P_{1,2}$).



So when the electron jumps from $L_2 \rightarrow K_1$, we get

	2P_1	2P_2
2S_1	$K\alpha'$ 1	$K\alpha$ 2

Similarly the origin of the L -spectra can also be explained. They arise when an electron is removed from any of the L -levels, and electron jumps from a higher level (M or N) to take its place.

If the above considerations be correct, it is perhaps wrong to say that the origin of X-ray spectra is similar to that of alkalis. The first term, arising from the presence of one electron in M is of course alkali-like. But the second pair of P -terms, arising from a defect of one electron from the completed L -level i.e. from the structure $2K_1 5L_2$, is halogenlike. Hence the difference $\nu_{K\alpha'} - \nu_{K\alpha}$ ought to be compared not to the value of $\Delta \nu$ between the two p -terms of alkalis (as is usually done), but to the $\Delta \nu$ -value of the normal levels of Halogens.

CONCLUDING REMARKS

With the systematisation of the data on complicated spectra a fresh crop of new problems suggest themselves to the theoretical physicist for solution (21). The future progress of theoretical physics must depend on the solution of these problems. We shall therefore examine the fundamental assumptions on which the interpretation of complex spectra has been built up. These are:

- (1) The fundamental spectrum (i.e. the spectrum given out by an electron revolving round a single nucleus) must be of a doublet type (one s -term, two p -terms, two d -terms, etc.).
- (2) Mechanical interpretation of different quantum numbers.
- (3) Explanation of Pauli's rule of exclusion.
- (4) Mechanical explanation of the principle of orbit synthesis.

It is rather remarkable that though the new developments in Quantum Mechanics viz.—Schrödingers' wave mechanics and Heisenberg's matrix mechanics, Dirac's non-commutative algebra—have made many points in the old quantum mechanics much clearer, they have scarcely been able to give a complete solution to any of the problems above mentioned. Let us take, for example, the first problem. The most satisfactory interpretation of the hydrogen spectrum is that of Schrödinger: following De-Broglie's ideas of the reconciliation between the wave theory, and the corpuscular theory of light, he has deduced an equation for the vibration of the hydrogen atom. It is shown that the hydrogen-atom can vibrate only when the negative energy takes up a number of discrete values made familiar by Bohr's theory. The theory has cleared

up the arbitrariness in Bohr's assumption of discrete quantum states, and has further given the quantum numbers correctly, for s , p , d , f -orbits, the value of $i_k=0$, 1, 2, 3 respectively.

But Schrödinger's theory explained only the singlet spectrum; but we know that the spectrum of hydrogen is a doublet spectrum. The reason for the discrepancy is to be sought in the assumption of the electron as a point-charge only, whereas we know that the electron possesses also a definite amount of magnetic moment equal to

$$\pm \frac{eh}{4\pi cm}. \text{ Pauli (22) has made an attempt to perfect}$$

Schrödinger's theory by taking the magnetic moment into account, but according to the author himself, the attempt has not yet been very successful. The usual equations of motion of the electron are now admitted to be imperfect, but the satisfactory equation is still to be found.

That the solution of the hydrogen spectrum offered by Schrödinger is still to be completed is also clear from the celebrated experiments of Stern and Gerlach on the deflection of atomic rays by a nonhomogeneous magnetic field. Recently these experiments have been extended to atomic rays of hydrogen (23) as well, and evidence has been obtained that the hydrogen atom in the fundamental

2S_0 -state possesses the magnetic moment of $\frac{eh}{4\pi cm}$. Now

according to Schrödinger, for the s -state, $i_k=0$ and the hydrogen atom would be nonmagnetic if magnetism arose from orbital motion alone. The magnetism which is actually observed, therefore, arises not from the orbital-motion (as originally supposed) of the electron, for according to Schrödinger's theory, such orbital motion does not exist in the case of the s -state. It must therefore be traced to the electron itself, as has been assumed by Goudsmit and Uhlenbeck in their hypothesis of the rotating electron. But Schrödinger assumes the electron to be a point charge only (1).

¹The assumption that the magnetic moment in atomic rays of H, Na or Cu, and Ag arise from the rotational motion of the valency electron, and not from their orbital motion clears up one very important objection raised against the theoretical understanding of Stern and Gerlach experiment by Einstein and Ehrenfest (Zs. für Physik, Bd II, page. 31). The atomic rays, as they enter the magnetic field, cannot have their magnetic axis in any definite direction. When they enter the field, the magnetic axis makes a precessional motion about the axis of the external field. This precessional motion gives rise to a radiation and a radiation damping. The time required by the damping factor to stop the precessional motion to rest, and align the magnetic axis of the atom parallel to the magnetic field was calculated by Einstein and Ehrenfest to be of the order of 10^{-15} sec., while the actual time of orientation must be $\leq 10^{-8}$ sec. But according to what has been said before, the electron, being a small magnet must execute not only a precessional motion, but also a nutational motion about the axis of the outer field. The moment of inertia of the electron being extremely small, the magnetic axis of the electron will soon set itself parallel to the outer field.

After hydrogen, the problem of the helium spectrum naturally suggests itself for solution. It is a time-honoured problem, and has baffled many attempts at solution. Recently solution on the basis of Schrödinger's theory have been published by Unsöld, Sugiura, and Kellner (24). Kellner has taken the calculations to the fourth place and finds an exact agreement between the theoretical and the experimental value. But this agreement does not exhaust all the points in the helium problem. One has to remember that the old Bohr theory gave the ionisation potential of hydrogen quite correctly, but it did not solve all the points in the hydrogen problem. In helium we have further to explain the origin of the parhelium and helium series, and the absence of inter combination amongst them. An explanation has been attempted by Heisenberg (25), and by Dirac, but both these authors have treated the electron merely as a point charge, while according to Hund's interpretation the difference in value between 1S and 3S is due only to the different orientation of the magnetic axis in the two cases. The 2 1S_0 -terms arises with electron (1) at K_1 , electron (2) at L_1 , but with its magnetic axis directed in an antiparallel direction. For the 2 3S_1 term, electron (1) is at K_1 , electron (2) at L_1 , but their magnetic axes are now parallel. The difference in value seems to be of magnetic origin and not to electrical origin, as supposed by Heisenberg and Dirac.

Wigner (26) has attempted a general explanation of the origin of different groups of terms in complicated spectra on the basis of Heisenberg's theory, but it is yet too early to pronounce a critical opinion on these works.

1. FOWLER, *Obituary Notice of Sir Norman Lockyer*, P. R. S. London, Vol. 104 (I).
2. SOMMERFELD, *Atombau und Spektral-linien*, Chap. 8.
3. SOMMERFELD, loc. cit., Chap. 8.
4. CATALAN, Phil. Trans. (A), vol. 222.
5. LANDÉ, in *Zeeman-Effekt und Multipletstruktur*, Berlin, 1925.
6. STONER, Phil. Mag., Bd. 48, 719.
7. SAUNDERS and RUSSELL, Astro. Journal, vol. 61, p. 38.
8. HEISENBERG, Zs. f. Physik, Bd. 32, p. 841.
9. HUND, Zs. f. Physik, Bd. 33, p. 345; Bd. 34, p. 296.
10. SCHRÖDINGER, *Abhandlungen zur Wellenmechanik*, J. A. Barth, Leipzig, 1927.
11. BORN, HEISENBERG, JORDAN, Zs. f. Physik, Bd. 35, p. 572.
12. DIRAC, Proc. R. S., London, vol. 113, p. 621, and other papers.
13. GOUDSMIT and UHLENBECK, Physica, 5, p. 266, 1925.
14. MILLIKAN and BOWEN, various papers in the 'Physical Review' from 1923, and in the Proceedings of the National Academy of Science, Washington.
15. SOMMERFELD and UNSÖLD, Zs. f. Physik, vol. 36, p. 262.
16. LAPORTE, J. O. S. A., vol. 13, page 1.
17. LAPORTE, loc. cit.
18. For Y, Zr, Nb, Mo see MEGGERS, J. O. S. A., vol. 12, p. 20; Ru and Rh, SOMMER, Zs. f. Physik, Bd. 37, p. 1; Bd. 45, p. 189; for Pd, J. C. MCLENNAN and H. G. SMITH, P. R. S., London, vol. 112, p. 110.
19. P. K. KICHLU and M. N. SAHA, Phil. Mag., Bd. 4, 1927, p. 193.
20. M. N. SAHA and B. B. RAY, Phys. Zeits., Bd. 28, p. 221.
21. O. W. RICHARDSON, *Presidential Address to the Physical Society of London*, vol. 39.
22. PAULI, Zs. f. Physik, Bd. 43, p. 601.
23. WREDE, Zs. f. Physik, Bd. 41, p. 569; PHIPPS and TAYLOR, Phys. Rev., Bd. 29, p. 309.
24. UNSÖLD, Ann. d. Physik, Bd. 82, p. 355; SUGIURA, Zs. f. Physik, Bd. 44, p. 190; KELLNER, Zs. f. Physik, Bd. 44, p. 91 and 110.
25. HEISENBERG, Zs. f. Physik, Bd. 39, p. 499; DIRAC, Proc. R. S. London, vol. 113.
26. WIGNER, Zs. f. Physik, Bd. 43, p. 424.

43(a). EXTENSION OF THE IRREGULAR DOUBLET LAW TO COMPLEX SPECTRA

M. N. Saha & P. K. Kichlu

(*Ind. Journ. Phys.*, **2**, 319, 1928)

The Irregular Doublet Law was discovered by G. Hertz in 1921.¹ It states that if the square roots of the values of the L_I and the L_{II} -absorption levels in X-ray Spectra are plotted against the atomic number, the two curves nearly run parallel to each other. Mathematically this means that

$$\sqrt{\nu_I} - \sqrt{\nu_{II}} = \text{constant} \quad \dots (1)$$

The explanation on Bohr's theory is that the energy of the electron in the L-level is given by

$$\frac{\nu}{R} = \frac{(Z - \sigma_I)^2}{n^2}, \frac{(Z - \sigma_{II})^2}{n^2} \text{ respectively}$$

where Z = nuclear charge

n = Total quantum number for L_I and L_{II}

σ_I = Screening constant while the electron is in the L_I -level

σ_{II} = Screening constant while the electron is in the L_{II} -level.

n has the same value in both cases, viz., 2.

$$\sqrt{\nu_I} - \sqrt{\nu_{II}} = \frac{\sigma_I - \sigma_{II}}{n} \quad \dots (1')$$

The extension of the Irregular Doublet Law to optical region is due to Millikan and Bowen.² Starting from a

¹ G. Hertz, Zs. f. Physik. Vol. 3, p. 19.

² Millikan and Bowen, Phy. Rev. Vol. 24, p. 209 (1924) and subsequent papers.

theoretical treatment of the L-spectra of light elements which fall in the ultra-schumann region, these authors have gradually extended this law to predict and locate the spectra of elements which are reduced by heavy electrical discharge to the one valence or the two valence state. For example, let us take the group:—Na, Mg^+ , Al^{++} , Si^{+++} ... they have got the K and L-rings complete, and only one electron in the M-ring (M_1) they differ only in the nuclear charge, which are respectively 11, 12, 13, 14, but the electronic constitution is the same. When this electron is further excited, it gives the same type (doublet) of spectra in the case of all elements. Millikan and Bowen's Law in its most general form states that when we compare the frequency of such lines of these successive elements, as arise from similar transition in which the total quantum number remains unchanged, they form an arithmetic progression. Thus let us compare the $^2S_1-^2P_1$ —lines of Na, Mg^+ , Al^{++} ... The net nuclear charges are 1, 2, 3 ... etc, but the number of screening electrons (excepting the valency electron) is the same (10), and they are probably oriented in the same way. Hence the frequency in the M-state is

$$\begin{aligned}\frac{\nu}{R} &= \frac{(Z-\sigma)^2}{3^2} \text{ for the electron in the } M_1 \text{ -orbit} \\ \frac{\nu}{R} &= \frac{(Z-\sigma')^2}{3^2} \dots\dots\dots M_2 \\ \therefore \frac{\nu 2S_1 - \nu 2P}{R} &= \frac{2}{3^2} (\sigma' - \sigma) Z - \frac{\sigma'^2 - \sigma^2}{9} \\ &= AZ + B \dots(2)\end{aligned}$$

because σ' , and σ have presumably the same value in the series of elements considered.

$\therefore$ the $\nu_{23}-\nu_{2p}$ lines will form an A.P. [see Table 2].

In the hands of Millikan and Bowen, and other workers, this law has been a very powerful instrument in the location of spectra of stripped atoms having (1) one valency electron; (2) two valency electrons, (3) three valency electrons (for a few special transitions only).

All the data which are scattered about in the papers of Millikan and Bowen, and other workers are collected in the tables below. The object of this paper is not only the compilation of these tables, which are very useful for workers in spectroscopy, but also to show that the law is capable of much wider application, so that even complicated spectra can be predicted, and exactly located. Incidentally, it might be mentioned that the wide applicability of Millikan and Bowen's law seems to us to be the most complete vindication of the values which Bohr assigned to the total quantum numbers for the different X-ray levels within the atom. There is an ambiguity on this point as regards optical spectra. For example, according to Bohr, the D-lines

of Na ought to be described as $3s-3p$ —lines with the formulae

$$3s-3p = R \left[\frac{(11-\sigma_s)^2}{3^2} - \frac{(11-\sigma_p)^2}{3^2} \right] \dots(3)$$

whereas in the optical method of classification we describe it, as (using Paschen's notation)

$$1s-2p = R \left[\frac{1}{(1+s)^2} - \frac{1}{(2+p)^2} \right] \dots(3')$$

Formula (3) can be made to reduce to (3'), but no systematic work on this line is known. The carrying out of this programme is very important for the elucidation of the origin of Rydberg sequence.

In order to give a general explanation of the ideas contained in this paper, we start with the atomic chart given by one of the authors sometime ago, which gives a unitary explanation of the origin of the periodic classification, of X-ray spectra, and of optical spectra in a graphical way, embodying the principle successively developed by Bohr, Mainsmith and Stoner, Pauli and Heisenberg and Hund.

[To get the spectrum of any element, write out the number of electrons, beginning from K. Let now the last electron run through the higher unfilled levels. We get the optical terms when we apply the principles of term-synthesis discovered by Pauli, Heisenberg and Hund.]

For more complete explanation, and application of this chart, the reader is referred to the previous papers by the senior author.³ Here we shall simply add, that as the total quantum number remains the same for all horizontal transitions, lines arising from such transitions in the case of all successive elements which are reduced by electrical discharge to the same electron configuration, will form an Arithmetic Progression. The law is not confined to one, two or three valence elements alone, but to elements with higher valency as well. The application to four, five, six, seven and eight valence elements, and other elements with complicated spectra is taken after these tables are completed, though in the latter case, the complexity of the spectra makes the application a bit difficult.

General explanation to Tables 1 to 8.

We have collected the data for one valence elements under the groups

- (1) Li, Be^+ , B^{++} , C^{+++} ... Ne^{+7}
- (2) Na, Mg^+ , Al^{++} , S^{+++} ... A^{+7} (2) K, Ca^+ ...
- (3) Cu, Zn^+ , Cd^{++} , Ge^{+++} ... Kr^{+7} (3) Rb, Sr^+ ...
- (4) Ag, Cd^+ , In^{++} , Sn^{+++} ... Xe^{+7} , (4) Cs, Ba^+ ...
- (5) Au, Hg^+ , Tl^{++} , Pb^{+++}

Even in these cases, some further niceties 'regarding the application of the law are introduced. They are discussed under the footnotes' in the case of each individual table.

³Vide M. N. Saha and B. B. Ray, Phys. Zeits, Vol. 28, p. 221; M. N. Saha, Phys. Zeits, Vol. 28, p. 469. P. K. Kichlu and M. N. Saha, Phil. Mag., Vol. IV, (1927), p. 193.

Transition Groups		Rare Earths		Trans. Group	
1		2		3	
K₁ 2		L₁ 2		L₂ 6	
L₁ 2		M₁ 2		M₂ 6	
M₁ 2		M₂ 6		M₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂ 6		N₃ 10	
N₁ 2		N₂			

One Valence Electron Systems

Group I. Li ... Ne⁺⁷Normal state L₁, total quantum number=2

TABLE 1.

Atomic number	Element	$L_1 \leftarrow L_2$ $S_1 - {}^2P_1$	2S_1	$L_2 \leftarrow M_2$ ${}^2P_2 - {}^2D_2$	Ionisation Potential	References
3	Li	14904 (17024)	43486 ..	16379 (49745)	5.37 ..	Fowler's Report, p. 97.
4	Be ⁺	31928 (16431)	146880 ..	66124 (81584)	18.14 ..	Bowen and Millikan, Phys. Rev. Vol. 28, p. 256.
5	B ⁺²	48359 (16122)	305938 ..	147708 (112458)	37.79 ..	Sawyer, J. O. S. A. Vol. 14, p. 287.
6	C ⁺³	64481 (15974)	520034 ..	260166 ..	64.23 ..	Millikan and Bowen, Nature, Vol. 114, p. 380.
7	N ⁺⁴	80455 (15913)			97.39 ..	Bowen and Millikan, Phys. Rev. Vol. 27, p. 144.
8	O ⁺⁵	96368			137.35	Ditto
9	F ⁺⁶	..			184.07	Ditto
10	Ne ⁷	..			..	..

N.B.—The law holds as the table shows for $2^2S_1 \leftarrow 2^2P_1$ i.e., $L_1 \leftarrow L_2$ transition only and not for the PD-lines *vide* the following groups because the transition is from $L_2 \rightarrow M_2$ i.e., the total quantum number increases by 1. For the remaining groups even PD lines forms an A.P.

Group II Na ... A⁺⁷Normal state 6L₂ M₁

Total quantum number=3

TABLE 2

Atomic Number	Element	M ₁ ←M ₂ ² S ₁ — ² P ₁	M ₂ ←M ₃ ² P ₃ — ² D ₃	M ₃ ←N ₄ ² D ₃ — ² F ₃	N ₃ ←N ₄ ² D ₃ — ² F ₃	² S ₁	I.P.	References
11	Na	16956	12199	5415	5492	41449	5.12	Fowler's Report on series in line spectra.
		(18713)	(23531)	(16893)	(14862)	..	..	
12	Mg ⁺	35669	35730	22308	20354	121267	14.97	Fowler's Report.
		(18011)	(26307)	(29350)	(20997)	..	..	
13	Al ⁺	53680	62037	51658	41351	229543	28.32	Paschen, Ann. der Physik Vol. 71, P. 154
		(17600)	(26635)	(42124)	(25289)	..	..	
14	Si ⁺	71280	88672	93782	66640	364177	44.95	Fowler, Phil. Trans. Vol. 225, p. 38.
		(17369)	(26083)	..	..	..	..	
15	P ⁺	88649	114755	..	..	..	..	Bowen and Millikan, Phys. Rev. Vol. 25, p. 295.
		(17217)	(25558)	..	..	..	..	
16	S ⁺	105866	140313	..	..	..	..	Ditto.
		(17132)	..	..	..	..	..	
17	Cl ⁺	123001	..	..	..	..	..	Ditto.
18	A ⁺⁷	..	..	..	..	..	..	Ditto.

The irregular doublet law holds not only for ²S₁—²P₁ lines (M₁←M₂), but also for ²P—²D lines (M₂←M₃), because the total quantum number is 3 for all these terms. It does not hold good for the first ²D—²F combination, because the transition is from M₃←N₄, n changes from 4→3.

Group III K ... M^{n+6} Normal state= $6M_3N_1$

Total quantum number=4

TABLE 3

Atomic Number	Element	$N_1 \leftarrow N_2$ $^2S_1 - ^2P_1$	2S_1	$N_2 \leftarrow N_3$ $^2P_3 - ^2D_2$	I.P.	References
19	K	12985 (12207)	35006	8492 (22933)	4.30	Fowler's Report.
20	Ca ⁺	25192 (11372)	95740	31425 (18299)	11.77	" *
21†	Sc ⁺²	36564 (10978)	..	49724 (18340)	24.6	Russell and Lang, Astro. Journ., Vol. 66, p. 13.
22	Ti ⁺³	47542 (10506)	..	68064	43.05	"
23	V ⁺⁴	58048 (8708)	..	..	..	Lang, Nature, July, 14, 1926.
24	Cr ⁺⁵	..	..	..	..	
25	Mn ⁺⁶	..	..	..	..	

*The first 2D term is given by the electron in M_3 with total quantum number 3, but the first 2P term has the total quantum number 4, we have therefore taken the 2nd number of the 2D sequence, for which $n=4$.

†In the case of Sc⁺, Ti⁺⁺ and other following elements,—the largest term is 2D with $n=3$, and not 2S with $n=4$. Hence the I.P. for Sc⁺ et seq., will refer to 2D -term.

Group IV Cu ... Kr^{+7} Normal state= $10M_3N_1$

Total quantum number=4

TABLE 4

Atomic Number	Element	$N_1 \leftarrow N_2$ $^2S_1 - ^2P_1$	2S_1	$N_2 \leftarrow N_3$ $^2P_3 - ^2D_2$	I.P.	References
29	Cu	30535 (17948)	62308 ..	19151 (28402)	7.66 ..	Fowler's Report, p. 111. ..
30	Zn ⁺	48483 (16678)	144890 ..	47553 (29649)	17.8 ..	Von Salis, Ann. der Phys. Vol. 76, p. 145. ..
31	Ga ⁺²	65161 (16153)	247797 ..	77202 (29302)	30.5 ..	Carroll, Phil. Trans. Vol. 225, p. 359. "
32	Ge ⁺³	81314 (18506)	368701 ..	106504 ..	45.3 ..	" ..
33	As ⁺⁴	99820	..	..	..	..
34	Se ⁺⁵	..	..	..	..	..
35	Br ⁺⁶	..	..	..	..	..
36	Kr ⁺⁷	..	..	..	..	..

In this case, the $^2L_3 - ^2F_3$ lines also obey roughly the Irregular Doublet Law, as the total quantum number is now 4 in both cases.

Group V Rb ... M_0^{+5}
 Normal state = $6N_2O_1$.
 Total quantum number = 5

TABLE 5

Atomic Number	Element	$O_1 \leftarrow O_2$ $^3S_1 - ^3P_1$	3S_1	$O_3 \leftarrow O_2$ $^3P_2 - ^3D_3^*$	I.P.	References
37	Rb	12579 (11136)	33689	6538 (22232)	4.14	Fowler's Report, p. 104.
38	Sr ⁺	23715 (10219)	88952	28770 (16655)	10.93	Fowler's Report, p. 132.
39	Y ⁺	33934 (9784)	157822	45425	19.41	Bowen and Millikan, Phys. Rev. Vol. 28, p. 923.
40	Zr ⁺	43718	238546		29.33	
41	Nb ⁺					
42	Mo ⁺					

Group VI Ag ... X_0^{+7}
 Normal state = $10N_2O_1$
 Total quantum number = 5

TABLE 6

Atomic Number	Element	$O_1 \leftarrow O_2$ $^3S_1 - ^3P_1$	3S_1	$O_3 \leftarrow O_2$ $^3P_1 - ^3D_1$	I.P.	References
47	Ag	29552 (14584)	61096	18271 (24798)	7.51	Fowler's Report.
48	Cd ⁺	44136 (13046)	140226	43069 (23865)	17.24	Von Salis, Ann. der Physik, Vol. 76, p. 145.
49	In ⁺	57182 (12374)	225690	66934	27.76	Carroll. Phil. Trans. Vol. 225, p. 388.
50	Sn ⁺	69556 (13418)	327261		40.2	
51	Sb ⁺	82974				
52	Te ⁺					
53	I ⁺					
54	Xe ⁺					

Group VII Au ... Nt⁺⁷
 Normal state: 10 O₃P₁.
 Total quantum number=6

TABLE 7

Atomic Number	Element	$P_1 \leftarrow P_1$ $^3S_1 - ^3P_1$	1S_1	$P_3 \leftarrow P_3$ $^3P_3 - ^3D_3$	I.P.	References
79	Au	37359 (14126)	74510	20784 (23589)	9.16	Thorsen. Naturwissenschaft. Vol. 25, p. 500 (1923).
80	Hg ⁺	51484 (12675)	153701	44373 (22019)	18.9	Carroll. Phil. Trans. Vol. 225, p. 389.
81	Tl ⁺²	64160 (12010)	248045	66392 (24804)	30.5	Ditto.
82	Pb ⁺³	76150	355963	91196	43.8	Ditto
83	Bi ⁺⁴					
84	Po ⁺⁵					
85						
86	Nt ⁺⁷					

Two-Valence Systems

The two-valence systems ought properly to begin with the group (He, Li⁺, Be⁺⁺ ...). But there is no data in this group beyond He, and Li⁺. The normal state is X₁ X₁, or s², the next state is X₁ X₂ or sp. The sp-combination gives rise to $^3P_{0,1,2}$ 1P_1 -terms, and in the transition X₁X₁ ← X₁X₂, we get $^1S_2 - ^3P_1$, $^1S_2 - ^1P_1$ lines. Both these lines form an Arithmetic Progression as shown in the tables which follow.

It also seems to be rather remarkable that the difference $^3P_1 - ^1P_1$, in the case of successive elements, roughly vary as the net nuclear charge. Thus we have⁴

$$\begin{array}{ll} \text{for Mg.} & ^3P_1 - ^1P_1 = 13181 \\ \text{,, Al}^+ & ^3P_1 - ^1P_1 = 22390/2 = 11195 \\ \text{,, Si}^{++} & ^3P_1 - ^1P_1 = 29850/3 = 9950 \end{array}$$

Similarly the $^3S_1 - ^3S_0$ differences arising from a X₁X₁ combination, seem to increase as the net nuclear charge

$$\begin{array}{ll} \text{Mg.} & ^3S_1 - ^1S_0 = 2305 \\ \text{Al}^+ & ^3S_1 - ^1S_0 = 4077 \\ \text{Si}^{++} & \text{,,} = ? \end{array}$$

[We have taken the second members of the sequence.]
 These facts should have some bearing on the

Heisenberg-Dirac⁵ theory of the bifurcation of two-valence spectra into singlets and triplets on the basis of electrical coupling of the two electrons.

The P $\bar{P}$ -lines). Taking the Mg.-group, they are seen to arise from the transition M₁M₂ ← M₂M₂, or in this process the lines owe their origin to the transition of the electron from the M₂M₂ (initial) to the M₁M₂ (final) or in a M₁ ← M₃ transition, leaving the outer electron fixed. We have called such transitions as "Inner transitions."

Two-Valence Electron Systems.

Group I He ... C⁺⁴
 Normal state: 2K₁.

TABLE 8

Atomic Number	Element	$4 \leftarrow L_2$ $^1S_0 - ^1P_1$	$4 \leftarrow L_3$ $^3S_1 - ^3P_1$	I.P.	References
2	He	4857	9231	..	Fowler's Report, p. 9.
3	Li ⁺	18209	34072	..	Schüler, Naturwissenschaft. 1924, p. 579.
4	Be ⁺²				No other element has yet been investigated.
5	B ⁺³				
6	C ⁺⁴				

⁴ Here again the second number of the 3D -sequence has been taken for all the elements, as in the group K, Ca⁺...

⁵ Heisenberg, Zs. f. Physik, p. 239; Dirac, Proc. R. S. L., Vol. 113, p. 261.

Group II: Be ... Ne⁺⁶
 Normal state: 2L₁
 Total quantum number=2

TABLE 9

Atomic Number	Element	L ₁ ←L ₂	L ₁ ←L ₃	L ₁ L ₂ ←2L ₃		¹ P ₁ ← ³ P	¹ S ₀	I.P.	References
		¹ S ₀ ← ¹ P ₁	¹ S ₀ ← ³ P ₁	³ PP ≥ ¹ P ₁ ← ³ P ₁		net nuclear charge			
4	Be	42565		37714 (23859)				9.5	Bowen and Millikan, Phys. Rev., Vol. 28, p. 251.
5	B ⁺	73396 (28956)	28966 (14558)	61573 (23481)	44430	22215	194326	24.2	Bowen and Millikan, Phys. Rev., Vol. 26, p. 316.
6	C ⁺²	102352	43524	85054 (23267)	58828	19609		45.5	Ditto.
7	N ⁺³			108321 (23172)					Bowen and Millikan, Phys. Rev., Vol. 26, p. 154.
8	O ⁺⁴			131493					Ditto.
9	F ⁺⁵								
10	Ne ⁺⁶								

It was shown by Sawyer and Beese (Nature, Dec. 26, 1925) that the value of P $\bar{P}$ group is the mean between (¹S←¹P) of any element and (²S←²P) of the next higher stage of ionisation of the element. See Kichlu and Saha, Phil. Mag., July, 1927, p. 198.

Group III: Mg ... A⁺⁶
 Normal state: 2M₁
 Total quantum number=3

TABLE 10

Atomic Number	Element	M ₁ ←M ₂	M ₁ ←M ₃	M ₁ M ₂ ←2M ₃	M ₂ ←M ₃	¹ P ₁ ← ³ P ₁	¹ S ₀	I.P.	References
		¹ S ₀ ← ¹ P ₁	¹ S ₀ ← ³ P ₁	3P ₁ $\bar{P}_1$	³ P ₁ ← ³ D ₁	net nuclear charge			
12	Mg	35051 (24794)	21870 (15584)	35982 (20711)	26086 (32009)	13181	61672	7.61	Fowler's Report, p. 116.
13	Al ⁺	59845 (23033)	37454 (15574)	56693 (20293)	58095 (31957)	11195	151860	18.74	Paschen, Ann. der. Phys., Vol. 71, p. 544.
14	S ₁ ⁺²	82878 (22312)	53028	76986 (20051)	90052	9 950	270170	33.35	A. Fowler, Phil. Trans., Vol. 225, p. 1.
15	P ⁺³	105190		97037					Bowen and Millikan, Phys. Rev., Vol. 25, p. 591.
16	S ⁺⁴	(21954) 127144 (21805)		(19948) 116985 (19943)					Ditto.
17	Cl ⁺⁵	148949		136928					Ditto.
18	A ⁺⁶								

Group IV: Ca ... Kr⁺⁶
 Metastable State M₃ N₁
 Total quantum number=4

TABLE 11

Atomic Number	Element	N ₁ ←N ₂ ³ D ₃ — ³ D ₂	N ₁ ←N ₂ ¹ D ₃ — ¹ D ₂	N ₂ ←N ₃ ³ D ₃ — ³ D ₂	¹ S ₀	I.P.	References
20	Ca	17870 (10084)	13985 (9555)		49305	6.06	Fowler's Report, p. 121, Russell and Saunders, Astro. Jour., Vol. 61, p. 38.
21	Sc ⁺	27954 (11015)	23540 (9954)				Goudsmit, Mark and Zeeman., Proc. Amst., Vol. 28, p. 127.
22	Ti ⁺²	38969	33494	52595			Russell and Lang, Astro. Journ., Vol. 66, p. 27.
23	V ⁺³						
24	Cr ⁺⁴						
25	Mn ⁺⁵						
26	Kr ⁺⁶						

Group V: Zn.....Br⁺⁵
 Normal state: 10M₃ 2N₁
 Total quantum number=4

TABLE 12

Atomic Number	Element	N ₁ ←N ₂ ¹ S ₀ — ¹ P ₁	N ₁ ←N ₂ ¹ S ₀ — ³ P ₁	³ PP	¹ P ₁ — ³ P ₁	I.P.	References
					net nuclear charge		
30	Zn	46745 (23952)	32502	47894 (19516)	14243	9.30	Fowler's Report, p. 140.
31	a ⁺	70697 (21179)		67410 (18738)			R. J. Lang, Phys. Rev., Vol. 30, P. 762.
32	Ge ⁺²	91876	45462	86148	15471	31.96	Ditto.
33	As ⁺³						
34	Se ⁺⁴						
35	Br ⁺⁵						

Group VI; Cd.....I⁺⁵
 Normal state: 10 N₃ 2O₁
 Total quantum number=5
 $O_1 \leftarrow O_2 \quad O_1 \leftarrow O_2$

TABLE 13

Atomic Number	Element	$^1S_0 \rightarrow ^1P_1$	$^1S_0 \rightarrow ^3P_1$	$^3P_1 \rightarrow ^3P_1$	1S_0	I.P.	References
48	Cd	43692 (19345)	30656	44088 (15810)	72539	8.95	Fowler's Report, p. 143.
49	In ⁺	63037 (16871)		59898 (15023)			R. J. Lang, Phys. Rev., Vol. 30, p. 769.
50	Sn ⁺²	79908	55191	74921	243235	30.0	Green and Loring, Phys. Rev., Vol. 30, p. 574.
51	Sb ⁺³						
52	Te ⁺⁴						
53	I ⁺⁵						

THE THREE-VALENCE ELEMENTS

The normal state is $2X_1X_2$ or s^2p^1 . The next stage is s^2d^1 or s^2s . The $^2P \rightarrow ^2D$ lines follow the law roughly in the group Al, Si⁺ etc. Data in other groups are incomplete.

The lines arising from the "inner transition" $2M_1M_2 \leftarrow M_12M_2$ follow the law more regularly.

Group I: B.....Ne⁺⁵
 Normal state: $2L_1 L_2$
 Total quantum number=2

TABLE 14

Atomic Number	Element	$L_2 \leftarrow M_3$ $^3P_2 \rightarrow ^3D_3$	$2L_1L_2 \leftarrow L_12L_2$		3P_1	I.P.	References
			$^3P_2 \rightarrow ^3D_3$	$^3P_2 \rightarrow ^3S_1$			
5	B	54751 (90798)	47841 (27026)		67545	8.34	Bowen, Phys. Rev., Vol. 29, p. 229.
6	C ⁺	145549 (121609)	74867 (25983)	96430 (34399)	196659	24.29	A. Fowler, Proc. Roy. Soc., Vol. 105, p. 299.
7	N ⁺²	267158	100850 (25699)	130829 (33152)	382226	47.2	Bowen, Phys. Rev. Vol. 29, p. 229.
8	O ⁺³		126549	163981		77.0	Ditto.
9	F ⁺⁴						
10	Ne ⁺⁵						

In the present group the first PD terms do not follow the law, as the transition is from 2 to 3 total quantum numbers. The inner transition ($L_1 \leftarrow L_2$) on the other hand follows the law.

Group 2: $Al \dots A^{+5}$
 Normal state: $2M_1 M_2$
 Total quantum number = 3

TABLE 15

Atomic Number	Element	$M_2 \leftarrow M_3$ $^3P_2 - ^3D_2$	3P	$2M_1 M_2 \leftarrow M_1 2M_2$ $^3P^2P$	I.P.	References
13	Al	32325 (46731)	48280	56615 (27102)	5.96	Fowler's Report, p. 156.
14	Si ⁺	79056 (37265)	131818	83717 (25134)	16.27	Fowler, Phil. Trans., Vol. 225, p. 1. PP groups from Al...
15	P ⁺	116321 (34868)		108851 (24441)		Cl ⁺ are given by Bowen and Millikan, Phys. Rev., Vol. 26, p. 160.
16	S ⁺	151189 (33200)		133292 (24111)		
17	Cl ⁺	184390		157404		
18	A ⁺					

In this group, the first PD lines follow the law roughly, the transition being from $M_2 \leftarrow M_3$. The P—S lines ($M_2 \leftarrow N_1$) do not obey the law at all.

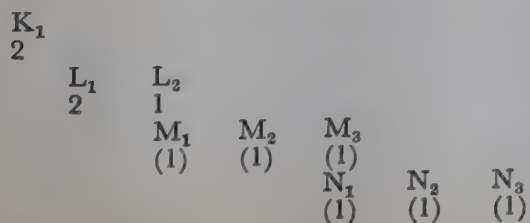
FOUR-VALENCE ELEMENTS

The several groups are

- (1) C, N⁺, O⁺⁺, Fl⁺⁺⁺...
- (2) Si, P⁺, S⁺⁺, Cl⁺⁺⁺...
- (3) Ge, As⁺, Se⁺⁺, Br⁺⁺⁺...
- (4) Sn, Sb⁺, Te⁺⁺, I⁺⁺⁺
- (5) Pb, Bi⁺, Po⁺⁺...

The knowledge of the spectra of these elements is very meagre except in the case of groups (1) and (11). In group (1) the spectrum of N⁺ has been almost completely analysed by Fowler and Freeman, while that of O⁺⁺ has been elucidated by Millikan and Bowen in the Schumann region, and by Mihul in the visible region. But our knowledge of the spectrum of Carbon proper is very meagre.

Let us see how the spectrum of Group (1) Carbon can be located with the aid of our knowledge of the spectrum of N⁺ and O⁺⁺. The structure diagram is



Full details of the expected terms, and their values in the case of N⁺, and O⁺⁺ will be found in a paper by Fowler, Proc. Roy. Soc., London, Vol. 117, p. 325.

It may be mentioned here that Millikan and Bowen have already shown that the law holds in the case of the inner transitions. Their figures are shown in the table below:

TABLE 16

Atomic Number	Element	$2L_1 2L_2 \leftarrow ^3P_1 - ^3S_1$	$L_1 3L_2 \leftarrow ^3P_1 - ^3P_1$	$^3P_2 - ^3D_2$	References
6	C	7	75239 (33930)	64046 (28074)	
7	N ⁺	155078 (41895)	109169 (33099)	92120 (27627)	
8	O ⁺	196973 (41151)	142268 (32753)	119747 (27487)	
9	F ⁺	238124	175021	147234	

Let us now try to apply the law to outer transitions as well. These are $L_2(M_1 \leftarrow M_2)$ and $L_2(M_2 \leftarrow M_3)$. Of the large number of lines arising from each, we have chosen only a few representative ones, both terms having the same inner quantum number.

TABLE 17

 $L_2M_1 \leftarrow L_2M_2$ $L_2M_2 \leftarrow L_2M_3$

Element	$3P_1-3P_1$	$3P_1-3D_1$	$1P_1-1P_1$	$3P_1-3P_1$	$3D_1-3D_1$
C	(10400)	(8673)	(9307)	(7331)	(8469)
N ⁺	21667	17581	25014	18301	20916*
	(11268)	(8908)	(15707)	(10970)	(12447)†‡
O ⁺⁺	32935	26489	40721	29271	33863
F ⁺⁺	(44000)	(35000)		(40000)	(46000)
Ne ⁺⁺					

From this table we can easily perceive why the spectrum of Carbon has up to this time remained unknown. The chief lines ($2L_2 \leftarrow L_2M_1$), $3P-3P$, lie in the Schumann region, as well as all other lines arising from deeper transitions. The lines arising from ($L_2M_1 \leftarrow L_2M_2$) lie in the region λ 9000 ... λ 12000 ($L_2M_1 \leftarrow L_2M_3$) lie in the region λ 11000 ... λ 13000.

Hence the spectrum of C must be investigated in the infra-red for the location of these lines. Other possible lines may be in the visible region but they would be extremely weak, and special methods of excitation will have to be employed to bring them out.

Though the systematisation of the spectrum of Carbon, and the exact value of its Ionisation Potential will depend upon the investigations above mentioned, it is not difficult to predict what the I.P. will be.

It is a general rule that the terms arising from the inner transition, viz., L_1 , $3L_2$ are in the case of neutral elements almost always negative, or at least have very small positive values. We have not much of exact data, but a glance at Table 14, which gives the inner transition lines of C, combined with a knowledge of corresponding term values for different electron configurations for N⁺ and O⁺⁺ should be sufficient indication that the value of $3P_1$ terms in C will be about 90,000, which corresponds to 11.0 volts approximately.*

Certain experiments with an Adam Hilger Infra-red spectrometer have shown that Carbon possesses strong lines in the regions predicted, but their fine structure has not yet been determined.

Group Si, P⁺, S⁺⁺, Cl⁺⁺⁺

The spectrum of Si has been discussed by Fowler, that of P⁺ by Bowen. In the case of S⁺⁺, and Cl⁺⁺⁺, certain vacuum spark data are recorded by Millikan and Bowen. The application of the Irregular Doublet Law is shown in the following table:

TABLE 18

 $M_2M_3 \leftarrow M_2M_2$ $M_2N_1 \leftarrow M_2M_2$ $2M_1$ $2M_2 \leftarrow M_1$ $3M_2$
Inner Transition

Element	$3P_1-3D_2$	$3P_1-3P_1$	$3P_1-3P_1$	$3P_1-3D_2$	$3P-3D$	References
Si	45216	50191				Fowler, Phil. Trans., Vol. 225
	(19890)	(26157)				
P ⁺	65106	76648	18558	16595	103726.6	Bowen, Phys. Rev.
	(18646)	(25583)				
S ⁺⁺	83752	(102231)				Millikan and Bowen, Phys. Rev. Vol. 23, p. 16.
Cl ⁺⁺⁺	(101546)	(126936)				

*Fowler has recently announced that the I. P. of C is 11.2 Volts. (Nature, Feb. 25, p. 304, 1928)

The identification of λ 1194, $\nu=83275$ as the $3P_1-3D_2$ line of S⁺⁺ seems to be well-warranted, the full multiplet being as given below

TABLE 19

	$3P_0$	$3P_1$	(737) $3P_2$
$3D_1$	84002		
D_2		(1) 83752	(1) 83015
D_3			(4) 83275

The line 978.2, $\nu=102231$, may be the $3P_1-3P_2$ line, but the wave lengths in this region ought to be revised. The chlorine lines are given provisionally. They require confirmation.

In the second table ($M_2N_1 \leftarrow M_2N_2$) transition, data are known in the case of P only. The Silicon lines must be in the infra-red. The existing data do not help us. The corresponding S⁺⁺ lines ought to lie in the region $\nu=26000-30000$, but they have not yet been looked for.

FIVE-VALENCE ELEMENTS

We have the following groups:

1. N,	O ⁺ ,	Fl ⁺⁺ ,	Ne ⁺³
2. P,	S ⁺ ,	Cl ⁺⁺ ,	A ⁺³
3. As,	Se ⁺ ,	Br ⁺³ ,	Kr ⁺³
4. Sb,	Te ⁺ ,	I ⁺⁺ ,	Xe ⁺³
5. Bi	Po ⁺		

The spectra of none of these elements, has been completely elucidated, O⁺ is a solitary exception, which has been treated by Fowler and Bowen; N has been done only partially. The Table 18 is given to indicate the region in which the line of Fl⁺ have to be looked for.

TABLE 20

FIVE-VALENCE ELEMENTS

 $2L_2(M_1 \leftarrow M_2)$ $2L_2(M_2 \leftarrow M_3)$

Element	$4P_2-4D_1$	$4P_2-4P_2$	$4P_2-4S$	$4D_2-4F_3$	$4D_2-4D_2$	$4D_2-4P_1$	References
N	11475	12175	13432				Kiess and Kiess, J.O.S.A. Vol. II, p. 1.
O ⁺	21346	23052	26822	24564	25960		
Fl ⁺⁺							Fowler, Proc. Roy., Soc. Lond. Vol. 110, p. 479.
Ne ⁺³							Bowen, Phys. Rev., Vol. 29, p. 243.

SIX-VALENCE ELEMENTS.

The groups are

1. O, Fl⁺, Ne⁺⁺
2. S, Cl⁺, A⁺⁺

3. Se, Br⁺, Kr⁺⁺
4. Te⁺, Xe⁺⁺

The application of the irregular Doublet Law to group 1 is shown in Table 21.

TABLE 21

 $(3L_2M \leftarrow 3L_2M_2)$ $(3L_2M_2 \leftarrow 3L_2M_3)$

Element	$5S_2-5P_2$	$3S_1-3P_1$	$5P-5D$	$3P-3D$	References
O	12859 13108	11836	10788 (17748)	8857	Fowler's Report.
Fl ⁺	25967 12578		28536		Discovered by D. S. Jog.
Ne ⁺⁺	38545				

The $^5S_2-^5P_2$ lines, transition $3L_2M_1 \leftarrow 3L_2M_2$ of Fl⁺, and Ne⁺⁺ have been obtained by Mr. D. S. Jog, following the indications of the irregular doublet law. The $^5P-^5D$ lines of Fl⁺ seem also to be correctly located. The elucidation of the spectra of Fl⁺ and Ne⁺⁺ will be very helpful to the understanding of the spectrum of O, which is now arousing wide interest owing to McLennan's discovery that the green auroral line must be due to O. A knowledge of the spectra of Fl⁺ and Ne⁺⁺ will help us in finding out the transition to which the green line owes its origin. The Oxygen spectrum itself is difficult, as the separations are very small, the quintets appearing as triplets, and triplets appearing as singlets.

SEVEN-VALENCE ELEMENTS

The groups are—

- (1) Fl, Ne⁺, Na⁺⁺, Mg⁺⁺⁺.....
- (2) Cl, A⁺, K⁺⁺, Ca⁺⁺
- (3) Br, Kr⁺, Rb⁺⁺, Sr⁺⁺⁺.....
- (4) I, Xe⁺, Cs⁺⁺, Ba⁺⁺⁺.....

The spectrum of Ne⁺ has been almost completely elucidated by the junior author. Subsequent work by De Bruin has confirmed his analysis. The spectrum of Fl has been analysed by De Bruin and Dingle but they have not yet been able to trace $^4L_2(M_2 \leftarrow M_3)$ -lines. They will be in the

infra-red. We are, therefore, in a very nice position to predict the spectrum of Na^{++} , but data is yet completely

wanting. The expected frequencies are shown within brackets in the following table.

TABLE 22

SEVEN-VALENCE ELEMENTS

Element	$4L_2M_1 \leftarrow 4L_2M_2$			$4L_2M_3 \leftarrow 4L_2M_2$			References
	$^4P_1 - ^4D_2$	$^4P_2 - ^4P_1$	$^4P_1 - ^4P_1$	$^4D_3 - ^4F_4$	$^4D_3 - ^4D_2$	$^4D_3 - ^4D_2$	
Fl	14628	13360	14025	..	..	..	Dingle, P.R.S.L., 113.
	(15418)	(13407)	(15567)	..	..	..	„ 117
Ne ⁺	30046	26747	29592	31579	29629	..	De Bruin, Zs. f. Physik, Vol. 40.
Na ⁺⁺	(45000)	(40000)	(45000)	..	..	..	P. K. Kichlu, Proc. Phys. Soc, Lond. Vol. 39, p. 424.
							No data available.

TABLE 23

EIGHT-ELECTRON ELEMENTS

Element	$5L_2(M_1 \leftarrow M_2)$			$5L_2(M_3 \leftarrow M_2)$			References
	$^3P_1 - ^3D_2$	$^3P_1 - ^3P_1$	$^3P_1 - ^3P_1$	$^3D_3 - ^3F_4$	$^3D_3 - ^3D_2$	$^3D_3 - ^3D_2$	
Ne	15798	16579	14883	11276	12105	..	Paschen and Götze, Serien-spektren.
	(16145)	(17614)	(16858)	(22271)	(21962)	..	M. N. Saha, Phil. Mag. Vol. 4, p. 223.
Na ⁺	31943	34193	31741	33547	34067	?	Majumdar's Analysis (Supra).
Mg ⁺⁺	(48000)	(52000)	(48500)	(55000)	(56000)	..	To be confirmed.

EIGHT-VALENCE ELEMENTS

The groups are—

- (1) Ne, Na⁺, Mg⁺⁺.....
- (2) A, K⁺, Ca⁺⁺....
- (3) Kr, Rb⁺, Sr⁺⁺....
- (4) Xe, Cs⁺, Ba⁺⁺....

In the following paper Mr. Kanakendu Majumdar describes his analysis of the Na⁺-spectrum. The spectrum of Na was treated as the mean between the spectra of Ne⁺ and Mg⁺, and the differences from that of Ne⁺ were predicted as the mean of the differences in the foregoing (Fl, Ne⁺)

and succeeding groups (Na, Mg⁺). The prediction has been very elegantly confirmed by Majumdar's analysis which is almost complete. The results are shown in Table 23. This enables us to predict the spectrum of Mg⁺ which is yet unknown. This is being investigated by Mr. Majumdar in this laboratory.

Summary.—In this paper, the full data of Millikan and Bowen's Arithmetic Progression Rule (Irregular Doublet Law in Optical Region) have been collected. The law has been extended to the case of complex spectra, and has been shown to hold good. Predictions are made regarding the spectra of certain elements which are yet unknown.

42(b) EXTENSION OF IRREGULAR DOUBLET LAW

M. N. SAHA & P. K. KICHLU

(*Nature*, **121**, 244, 1928)

Recent work in this laboratory has shown that the irregular doublet law, first discovered in 1920 by G. Hertz in the X-ray region, and since then extended by Millikan and Bowen for the optical region is capable of much wider application. Millikan and Bowen have applied the law for the prediction and identification of spectra of atoms which are stripped to one or two valency electrons by vacuum discharge, and in the case of higher valence elements, for inner transition lines. But the law can be applied for the prediction of spectra of elements with a larger number of valency electrons giving rise to complicated spectra. The extension of the law in its most general form can be thus enunciated:

If we compare the spectra of a group of successive elements which are reduced by electric discharge to the same electronic constitution (for example, C, N⁺, O⁺⁺, Fl⁺⁺⁺, N⁴⁺), then frequencies of corresponding lines arising out of a transition in which the total quantum number remains unchanged will form an arithmetic progression.

The law can be very easily illustrated with the atomic chart given by one of the authors (*Phys. Zs.*, p. 470; 1927).

K_1			
2			
L_1	L_2		
2	1		
	M_1	M_2	M_3
	[1]	→ (1)	→ (1)

In this chart, horizontal transitions refer to $\Delta n=0$. Thus taking C, N⁺, O⁺⁺ ... we find that the origin of

all possible groups of lines can be visualised as follows:

$$L_2L_2 \longrightarrow L_2M_1 \longrightarrow L_2M_2 \longrightarrow L_2M_3$$

$$(M_1 \longrightarrow M_2) \quad (M_2 \longrightarrow M_3)$$

Now the corresponding lines of the successive elements arising out of the transitions

$L_2M_1 \longrightarrow L_2M_2$, that is, $(^3P, ^1P) - (^3D, ^1\bar{D}, ^3\bar{P}, ^1S)$ lines, and

$L_2M_2 \longrightarrow L_2M_3$, that is, $(^3D, ^3\bar{P}, ^3S) - (^3F, ^3\bar{D}, ^3P)$

will form arithmetic progressions.

Application of this law can be extended to all other complicated spectra.

It follows that if the spectra of two elements, preferably successive, of any group be known, it becomes quite easy to predict the spectra of the remaining elements.

In the group just mentioned, namely, C, N⁺, O⁺⁺ ... the spectra of N⁺ has been completely elucidated by Fowler and Freeman, and that of O⁺⁺, is nearing completion thanks to the work of Mihul. (Mihul's levels are wrongly given, though his multiplets are correct. They can be easily reshuffled and correctly fitted to Hund's theory.) We can then predict the spectra of C, which is still unknown. Then $L_2(M_1 \longrightarrow M_2)$, as well as $L_2(M_2 \longrightarrow M_3)$ lines which are next in intensity to the fundamental $L_2L_2 \longrightarrow L_2M_1$ ($^3P, ^1\bar{D} ^1S$) - ($^3\bar{P}, ^1\bar{P}$) lines are found to be beyond 8000 Å.

In a similar way, spectra of all groups can be predicted and correctly located.

Department of Physics,

Allahabad University,

Jan. 11.

43. THE ORIGIN OF NEBULIUM SPECTRUM

(*Nature*, **121**, 418, 1928)

In a letter to NATURE of Oct. 1, 1927, p. 473, Mr. Bowen has announced the very interesting relationship that some of the lines of unknown origin which are found in the nebulae and in the Wolf-Rayet stars and were so long

attributed to a hypothetical element nebulium, are really due to ionised light elements like O⁺⁺, N⁺⁺, O⁺, N⁺ ...; they do not arise from the transitions usually allowed, but are due to transitions which are usually prohibited.

Prof. A. Fowler has also lent his support to this hypothesis. The object of this note is to discuss the nature of these transitions.

Mr. Bowen finds that the following well-known trio of nebulium lines are due to O^{++} , and due to transitions shown below:

5006.84	.	.	.	.	$^3P_2-^1\bar{D}_2$
4958.91	.	.	.	.	$^3P_1-^1\bar{D}_2$
4363.21	.	.	.	.	$^3P_1-^1\bar{S}_0$

The structure diagram of O^{++} is shown below:

$$O^{++} \dots 2K \ 2L_1 \ L_2$$

$$M_1 \longrightarrow M_2 \longrightarrow M_3$$

$2L_2(p^2)$ gives us $^3P_{0,1,2}$, $^1\bar{D}_2$, $^1\bar{S}_0$.

All other four-valence elements, namely, C, N^+ , O^{++} , ... and C, Si, Ge, Sn, Pb have similar ground levels due to the electron-configuration p^2 , that is, two electrons in p - (or L) orbits. The lines arise from transitions between metastable levels as pointed out by Bowen. It is interesting to note that though such transitions are not found in the spectra of light elements, they are of frequent occurrence in the spectra of heavy elements. In the spectrum of Pb, which is analogous to that of O^{++} , the values of the fundamental levels are

3P_0	3P_1	3P_2	$^1\bar{D}_2$	$^1\bar{S}_0$
59821	52004	49173	38365	30355

Dr. Sur (*Phil. Mag.*, vol. 2, p. 623; 1926) in this laboratory found that the following lines exactly analogous to the above-mentioned nebulium lines are obtained in the heavy arc of lead. They are not present in the usual arc:

$$^3P_1-^1\bar{D}_2 = \nu 13637, \quad \lambda = 7330 \text{ A.}$$

$$^3P_1-^1\bar{S}_0 = \nu 21649, \quad \lambda = 4618 \text{ A.}$$

Other elements of the same group, namely, C, Si, Ge, Sn, can theoretically give similar lines, as the following Table shows, but a scrutiny of the existing literature shows that they have not yet been obtained. Whether they can be obtained in the heavy arc is yet to be seen.

$^3P_1-^1\bar{S}_0$ for C	.	.	.	.	?
Si	.	.	.	.	$\nu 15317$
Ge	.	.	.	.	$\nu 15810$
Sn	.	.	.	.	$\nu 19101$

Let us now consider the nature of violation of the selection principle. I have shown that in the case of complex spectra the selection principle can best be explained not in terms of the different quantum numbers, but in terms of *electron transition*. Thus $pp \rightarrow ps$ or $pp \rightarrow pd$ transitions are allowed (one electron changing from the p -orbit to the s -orbit, or the d -orbit, corresponding to $\Delta k = \pm 1$ where $k = \text{azimuthal quantum number}$), but $pp \rightarrow pp$ transitions are not allowed ($\Delta k = 0$). In terms of the structure diagram, this means that only those transitions are allowed in which the total number of electron transition is odd. Hence the transition involved in the origin of the nebulium lines really violates the selection principle $\Delta k = \pm 1$; we have here $\Delta k = 0$, and in addition $\Delta n = 0$ (change of total quantum number $n = 0$).

It is well known from the experiments of Koch on helium and other subsequent experiments, as well as from theoretical considerations, that such violations take place when the region where the spectrum is produced is traversed by a big electric field, or in regions where the free charge density is high. In heavy elements, the principle is easily violated, because the central atomic field deviates largely from the radial. A big external electric field, or free electric charges, would help the process, where such internal fields are not present, as in light elements, or are insufficient. Such, in fact, is the interpretation to be put on Dr. Sur's results. Similarly, in other heavy elements, namely, Bi, Th, Au, prohibited transitions of this type are very frequent.

Bowen's interpretation of the nebulium lines as being due to prohibited transitions in light elements therefore implies that unusually big electric fields are present in nebulae and Wolf-Rayet stars. This can be explained, because, owing to the extremely high temperature, matter must be in a very highly ionised state, and large fluctuations of electrical density, owing to accumulation of charges of one sign, must be very frequent. Bowen further finds that besides these lines, lines due to the transitions $L_2M_1-L_2M_2$ and $L_2M_2-L_2M_3$ of O^{++} are obtained in these stars. The fact that the electron, while returning from the higher excited group of orbits (due to L_2M_2), appears to linger too long in the less stable $^1\bar{D}_2$ of the L_2L_2 combination, is to be attributed to this big electric field.

The University, Allahabad.

44. THE ORIGIN OF THE SPECTRUM OF THE SOLAR CORONA

(*Nature*, **121**, 671, 1928)

THE arguments which have been brought forward to explain the origin of the spectra of nebulae may be used with certain modifications to explain the spectrum of the solar corona; for it must be composed of such atoms thrown out by radiation pressure or other agencies from the general atmosphere of the sun. On account of the lower temperature of the sun, the atoms concerned should be non-ionised, or such as can be easily ionised. They should also be light. All these considerations narrow down the choice to a very few elements like Li^+ , Be^+ , B^+ , C , N , O ... Si , P , S ; P^+ , and S^+ , etc. It is the object of this note to discuss how these elements can give rise to the coronal spectrum.

It is now generally recognised that matter above the solar photosphere is largely supported by radiation pressure acting in a selective way. Prof. Milne has shown from transition probabilities of the Ca^+ -atom (or the average life), that Ca^+ emitting the H - K lines is subjected to such a large radiation pressure that it almost overcomes the force of gravity. If this argument be true, the logical consequence would be to extend it to other elements. We can leave out H and He because their resonance lines are in the extreme ultraviolet and their normal atoms would be subjected only to slight radiation pressure. But such is not the case with Li . The resonance line of Li is at $6708 \text{ \AA}$, the corresponding $E_\lambda = 0.8 E_m$, the maximum emission E_m of the sun regarded as a black body at 6500°K ; hence the force of radiation would more than balance the force of gravity; it would be expelled entirely from the solar atmosphere. It can be retained only in the ionised form. The entire absence of Li -lines from the Fraunhofer spectrum seems to support this view. If Li^+ be present, it may or

may not be detectable, as the fundamental lines are in the Schumann region, and the excitation required to bring out the next important lines will be too large. The only favourable line is $\lambda 5484.69$, or $\lambda 5484.90$ (Rowland's Scale—a very weak line is given at 5484.846 in Rowland's Table, but the identification is doubtful), which belongs to the singlet system of $\text{Li}^+(2S-3P)$. Similar considerations would apply to Be^+ and B^+ .

In carbon we come across a new feature. This new feature is best explained by taking the case of Si , for which the full details of the spectrum are known. Si has five fundamental levels, $^3P_{012}$, 1D_2 , 1S_0 , all arising out of the combination pp (or M_2M_2). The next combination is ps (M_2N_1), and it gives rise to $^3P_{012}$, 1P_1 . The lines are shown in the accompanying table, the figures being taken from Fowler, *Phil. Trans.*, vol. 225, p. 45. The table shows that the ($^3P-^3P$) lines are the most fundamental, but their wave-length is at $\lambda 2514-2528$, while the less fundamental $^1S_0-^1P_1$, $^1S_0-^3P_1$ lines are at $\lambda 4103$, $\lambda 3905$. Si is in fact detected in the sun by those two lines, some other subordinate lines, and some lines of Si^+ . The problem now arises that if we heat Si to incandescence, to say 4000°C ., so that the corresponding wave-length of the maximum emission is towards the red, will the group at $\lambda 2514-2517$ be more intense or the lines $\lambda 4102$, $\lambda 3905$? Laws of temperature radiation demand that $\lambda 4102$, $\lambda 3905$ will be more intense, while the theories of spectra require that $\lambda 2514-2528$ will be more intense at all temperatures, as the $^3P_{012}$ states will be much more numerous than the 1S_0 -states ($n_{1S} n_{3P} = e^{-\frac{22000}{T}}$), and there is always a greater tendency on the part of the higher excited $^3P_{012}$, 1P_1 states to revert to the more fundamental state.

$\frac{L_2L_2}{L_2M_1}$	3P_0	3P_1	3P_2	1D_2	1S_0
3P_0		2524.118 39605.89(8)			
P_1	2514.331 39760.04(7)	2519.210 39683.03(7)	2528.516 39537.01(9)	2987.65 33461.39	4102.945 24365.89(5)
P_2		2506.904 39877.83(9)	2516.123 39731.73(10)	2970.35 33656.27(1)	
1P_1	2438.782 40991.64(3)	2443.378 40914.54(3)	2452.136 40768.42(3)	2881.585 34692.97(10)	3905.515 25597.61(9)

An experiment was performed at this laboratory by Messrs. Majumdar and Kichlu to decide this question. They did not work with silicon, but with the more easily manageable thallium. This has two fundamental states, $2p_1$, $2p_2$, separated by a large interval $\nu = 7793$, so that $n_2 p_2 / n_1 p_1 = \frac{1}{2} e^{-\frac{25011}{T}}$. They heated thallium in a vacuum graphite furnace to about 2500°A . and photographed the spectrum of thallium vapour. The $2p_1-3s$ line has the wave-length $\lambda 3775.72$, the $2p_2-3s$ line has the wave-length $\lambda 5350.46$. As the $2p_1$ state is about a hundred times more in abundance, we expected that the line $\lambda 3775.72$ would be more intense; at any rate it would not have less than half the intensity of $\lambda 5350.46$ (because the weights of $2p_1$ and $2p_2$ states are as $1:2$). But $\lambda 5350.46$ was at least ten times more intense than $\lambda 3775.72$. This fact is therefore more in accordance with the view that thallium vapour is partly in equilibrium with temperature radiation from the walls. But still we have to find out why the larger proportion of the $2p_1$ -atoms is maintained. This is met by assuming that the prohibited transition $2p_1-2p_2$ occurs in large proportion—in other words, under the influence of the existing field of radiation, most of the thallium atoms in the $3s$ -state return first to the $2p_2$ -state, and then from the $2p_2$ -state they return by the prohibited transition to the $2p_1$ -state, so that the equilibrium between the proportion of atoms between the $2p_1$ - and $2p_2$ -states is maintained by the prohibited transition, which marks the emission of the line $\nu = 2p_1 - 2p_2$.

Turning now to the case of silicon in the sun, we find that the same argument can be applied. The emissivity of the sun is almost a maximum at $\lambda 4102$ and $\lambda 3905$; at $\lambda 2500$, the emissivity is about 0.57 of the maximum. When silicon atoms are traversed by a radiation field of this type, we shall find that transitions corresponding to the emission of $1S_0-1P_1$, $1S_0-3P_1$ of silicon will be very frequent, while the transitions $3P_{012}-3P_{012}$ will be too small. The proportion between the fundamental $3P$ and metastable $1D_2$, $1S_0$ levels will be maintained by the prohibited transitions $3P_1-1S_0$, $3P_{12}-1D_2$. Also it follows that if the transitions from the excited $1P_1$, $3P_1$ -state to the $1S_0$ -state are as numerous as in the case of calcium, then silicon, being much lighter than calcium, would be thrown out into the corona in the metastable state $1S_0$. Hence the coronal spectrum would show the prohibited transition.

If these hypotheses regarding the presence of silicon are correct, we should expect the following deductions to be verified:

(1) The Fraunhofer spectrum of the sun should show the line corresponding to $3P_1-1S_0$, $\lambda = 6527.05$ (Rowland Scale). Rowland's table shows a line at $\lambda 6526.89$, intensity zero. The agreement is not satisfactory.

(2) The coronal spectrum should also show this line. There is a line of approximately this wave-length in Father Cortie's table of coronal lines; the wave-length is given as $\lambda 6528.9$.

(3) The silicon lines $\lambda 4103$ and $\lambda 3905.67$ should be high chromospheric lines. This is not quite confirmed; in Mitchell's tables they are stated to reach only heights of 500 km . and 800 km . This may be due to paucity of transitions from the $1P_1$ -state to the $1S_0$ -state.

Excited silicon atoms may or may not (in the $1S_0$ -state) form a constituent of the corona. But the above arguments will apply to other suitable elements. I have chosen silicon for illustration because we know all about its spectrum. The same cannot be said of carbon, nitrogen, and oxygen, to which similar arguments can be applied, because in these cases the differences in value between the metastable states are only roughly known. To take carbon; this has an ionisation potential of about 11.3 volts ; the spectrum is in all respects similar to silicon. The fundamental $3P-3P$ lines are at $\lambda 1656-1658$, but the metastable $1S_0-1P_1$ -line is probably the line $\lambda 2478$. Hence it can be stated that metastable carbon atoms, being very light, would be thrown into the corona, and there give rise to prohibited transitions $3P_1-1S_0$, $3P_{12}-1D_2$. The electrical field in the corona would increase the number of transitions. The frequencies of such lines are of the same order as the frequencies of the more intense coronal lines, but whether they agree absolutely will depend upon the exact determination of the value of these terms.

Similar, prohibited transitions between the fundamental levels of N and O, P and S, P^+ and S^+ , may account for some of the coronal lines. The present spectroscopic knowledge of the metastable states of these elements is so meagre, and the wave-lengths of the coronium lines are so roughly known, that I have not yet tried to institute any search for their origin amongst these states.

45. NEGATIVELY MODIFIED SCATTERING

M. N. SAHA, D. S. KOTHARI AND G. R. TOSHNIWAL

(*Nature*, **122**, 398, 1928)

IN a paper published in 1923, Einstein and Ehrenfest discussed the general problem of thermodynamical equilibrium in an assembly traversed by light, which is subjected to scattering by the particles of the assembly. They deduced, in a way (which is quite analogous to Einstein's famous deduction of the laws of black body radiation by consideration of thermodynamical equilibrium in the presence of Bohr type of vibrators), that the excited particles of the system would give rise to a type of modified scattering analogous to Einstein's negative absorption. Smekal pointed out in a letter to *Naturwissenschaften* (1923) that if light of frequency ν is scattered by the particles of the assembly, then in addition to unmodified scattering of frequency ν , scattered light should also consist of light of frequency $\nu + \nu_k$, $\nu - \nu_k$, where $h\nu_k$ is the energy difference between the excited state and the normal state of the scattering particles ("Handbuch der Physik," Bd. 23, pp. 93-99).

This last prediction has been very brilliantly confirmed by Raman and Krishnan, who exposed liquid benzene to the monochromatic mercury radiation $\lambda 4358$, and on examining the spectrum of the scattered light found modified scattered light of frequencies $\nu + \nu_k$ where ν_k is any one of the fundamental frequencies of liquid benzene. We wish to point out that Raman and Krishnan's experiment is not, strictly speaking, a confirmation of Einstein's negative or stimulated emission, as mentioned by these authors (*NATURE*, June 30, 1928), but of the analogous case of negatively modified scattering (that is, scattering of light of frequency $\nu + \nu_k$) discussed by Smekal.

We wish further to point out that the theory of modified scattering affords a very simple and convincing explanation of the phenomena of resonance spectra of vapours of sodium, potassium, and the halogens discovered and so elaborately described by R. W. Wood in his numerous papers. He found that when vapour of these substances is illuminated by monochromatic light (lithium, cadmium, bismuth, or zinc arc), then the vapour emits laterally a partially polarised spectrum consisting of the original line, and a number of fine lines spaced at equal frequency intervals (of about 145 in the case of Na). The position of these excited lines in the spectrum depends upon that of the exciting light, though the frequency interval between the exciting line and its adjacent excited light is independent

of the exciting frequency for the same substance. The remarkable fact is that there are also a number of lines on the shorter wavelength side of the exciting light, which have been styled by the German authors (Pringsheim and his students) the 'anti-Stokes' lines. These 'anti-Stokes' lines also show equal spacing, and they can be explained as being due to negatively modified scattering.

Pringsheim and his students have shown that the sodium vapour contains temporary Na_2 molecules and gives rise to banded spectra on excitation. One of the strongest vibration frequency intervals is $\Delta\nu = 145$, which may be identified with the frequency of one of the fundamental modes of vibration of the component atoms. So the explanation of Wood's resonance spectra becomes evident now. When the exciting light traverses Na_2 molecules, the light is scattered by them, the scattered light having the frequencies $\nu \pm \nu_k$ where $h\nu_k$ is the energy difference between any excited state and the normal state of the Na_2 molecule; the excitation not involving the electron displacement, but being due only to the vibration of the component atoms which are easily produced under moderate heating. The plus sign refers to the negatively modified scattered light and accounts for the anti-Stokes' lines. Similar explanations hold good for the resonance spectra of K_2 and the halogens. These substances alone have been shown to be capable of giving rise to resonance radiation, as the molecules can be easily excited to higher vibration frequencies. But it can presumably be proved to be a general phenomenon in the case of all molecules.

We wish further to point out that though the phenomenon has been described as one of 'scattering', it seems to be intermediate between pure scattering (as by fog-particles in which the agent responsible for scattering does suffer no physical change) and pure absorption (as, for example, the absorption of the sodium line by the sodium atom, resulting in the utilisation of the total energy of the energy-particle in lifting the electron to the higher orbit and production of a new system). This phenomenon is just intermediate between the two, as the incident light reacts on the particle, and robs it of its internal energy and is re-emitted as a new radiation of increased frequency.

It seems that the polarisation of the secondary rays is probably only a time effect, depending upon the intimacy

of the reactions taking place between the incident light and the scattering particle. Therefore in pure scattering, the scattered light should be completely polarised in pure absorption and in re-emission unpolarised; and in phenomena intermediate between these two it should be partially polarised, as has been proved by Wood.

The phenomena of negative scattering should also

be capable of extension to free electrons, and will thus probably afford an easy explanation of the origin of bright and broad bands in the spectra of Novae, and of winged lines in the solar spectrum.

Department of Physics,
Allahabad University, Aug. 14.

46. ON THE METHOD OF HORIZONTAL COMPARISON IN THE LOCATION OF SPECTRA OF ELEMENTS

M. N. SAHA AND K. MAJUMDAR

(*Ind. Jour. Phys.*, **3**, 67, 1929)

For sometime past workers in spectroscopy in this laboratory are using a new principle in the location of spectra of elements, which, in the absence of a better name, may be styled the method of Horizontal Comparison. To explain the method, we start with Table I, where, in the first row, we have taken the successive elements, B, C, N, O, F, Ne, and Na (atomic numbers 5 to 11). The K- and L₁-rings of these elements are complete but the number of electrons in the L₂-orbit in the normal state varies from 1 to 6 from B up to Ne; in Na there is one more electron in M₁ besides the full quota of 6 in L₂. The optically excited states are obtained by allowing one electron to run through the higher orbits. If x denotes the number of electrons in the L₂-orbit, the different optically excited states can be represented by

$xL_2M_1, xL_2M_2, xL_2M_3, xL_2M_4, xL_2M_5$, etc.

It is apparent that in the elements B to Na, x varies from 1 to 6.

In the second row, we have put the elements C⁺, N⁺,..... Mg⁺, and in the third row the elements N⁺⁺, O⁺⁺,...Al⁺⁺, so that elements in the same vertical column have the same electronic configurations, the nuclear charge increasing by one in each step.

TABLE I

$x \rightarrow$	0	1	2	3	4	5	6
I	B	C	N	O	F	Ne	Na
II	C ⁺	N ⁺	O ⁺	F ⁺	Ne ⁺	Na ⁺	Mg ⁺
III	N ⁺⁺	O ⁺⁺	F ⁺⁺	Ne ⁺⁺	Na ⁺⁺	Mg ⁺⁺	Al ⁺⁺

The elements in the same vertical column, *e.g.*, C, N⁺, O⁺⁺, follow the arithmetic progression law, when the transition is along the same horizontal level, that is, when the transition

takes place between orbits having the same total quantum number, *e.g.*, M₁←M₂. Recently this case has been exhaustively discussed by Prof. M. N. Saha and Dr. P. K. Kichlu¹ who have shown the validity of the law to higher valence elements. The purpose of the present paper is to compare the corresponding lines of the elements in the same horizontal row in table I. We shall at present confine our attention to the transition $xL_2 (M_1 \leftarrow M_2)$.

Owing to the variety of the electronic configurations of these elements, the nature of the lines involved is widely different. We shall, therefore, for the sake of simplicity, chose lines which arise from terms of the highest multiplicity. As for example, according to the Hund's theory, we expect the following terms in oxygen,—

$$\begin{aligned}
 3L^2M_1 & \left\{ \begin{array}{l} {}^5S \quad {}^3S \quad {}^3D \quad {}^3P \\ \quad \quad \quad {}^1D \quad {}^1P \end{array} \right. \\
 3L_2M_3 & \left\{ \begin{array}{l} {}^5P \quad {}^3P \quad {}^3F \quad {}^3D \quad {}^3P \quad {}^3D \quad {}^3P \quad {}^3S \\ \quad \quad \quad {}^1F \quad {}^1D \quad {}^1P \quad {}^1D \quad {}^1P \quad {}^1S \end{array} \right.
 \end{aligned}$$

which will give rise to a very large number of lines. As it is not possible to compare all the lines due to the above transition,—most of them have yet to be discovered,—we have taken only the quintet lines ${}^5S \rightarrow {}^5P$, which are also the strongest in the transition. In Chart I are collected the lines (of the highest multiplicity) of the corresponding elements given in Table I, due to the transition M₁←M₂. We have chosen from a multiplet only one line which has the average of the frequencies forming the multiplet. In the case where the average frequency does not much differ from the frequency of the strongest line in the multiplet, the latter frequency has been taken.

¹ Saha and Kichlu, *Ind. Jour. Phys.*, **2**, (1928).

CHART I

 $xL_2 (M_1 \leftarrow M_2)$

$x \rightarrow$	0	1	2	3	4	5	6
(1)	..	$^3P_2 - ^3D_2$	$^4P_2 - ^4D_2$	..	$^4P_2 - ^4P_2$	$^3P_1 - ^3S_1$	..
(2)	$^2S_1 - ^3P_1$	$^3P_2 - ^3S_1$	$^4P_2 - ^4P_2$	$^5S_2 - ^5P_2$	$^4P_2 - ^4D_2$	$^3P_2 - ^3D_2$	$^2S_1 - ^3P_2$
(3)	..	$^3P_2 - ^3P_2$	$^4P_2 - ^4S_2$	..	$^4P_2 - ^4S_2$	$^3P_1 - ^3P_2$	..
I	B	C	N	O	F	Ne	Na
(1)	..	..	11475	..	13360	13798	..
(2)	[6000]	10348	12175	12860	15582	15615	16973
(3)	..	10993	13433	..	15747	16399	..
		Fowler, P.R.S., 118, 42 (1928).	Kiess, J.O.S.A. 11, 4 (1925).	Fowler, Report, p. 168.	Dingle, P.R.S., 113, 326 (1927).	Saha, Phil. Mag. 4, 223, (1927).	Fowler, Report, p. 99.
II	C ⁺	N ⁺	O ⁺	F ⁺	Ne ⁺	Na ⁺	Mg ⁺
(1)	..	17602	21446	..	26767	27530	..
(2)	15198	19816	23052	25967	29977	32323	35761
(3)	..	21590	26821	..	33004	34411	..
	Fowler, P.R.S., 105, 306 (1924).	Fowler and Freeman, P.R.S., 114, 665 (1927).	Fowler, P.R.S., 110, 484 (1926).	Jog. Ind. Journ. Phy. 2, 344 (1928).	Kichlu, (Lond.) Phy. Soc., 39, 424 (1927).	Majumdar, Ind. Journ. Phy. 2, 353 (1928).	Fowler, Report, p. 120.
III	N ⁺⁺	O ⁺⁺	F ⁺⁺	Ne ⁺⁺	Na ⁺⁺	Mg ⁺⁺	Al ⁺⁺
(1)	..	26589	..	..	..	..	..
(2)	24399	29925	[34700]	38545	[44300]	[49000]	53918
(3)	..	32808	..	..	..	..	Paschen Ann. Phys. 71, 151 (1923).
	Bowen, Phy. Rev. 29, 234 (1927).	Fowler, P.R.S., 117, 325 (1928).		Jog. do.			

It will be evident from the chart that the frequencies in the same horizontal row increase with increase of atomic numbers. The relation has been graphically represented in fig. 1, where we find that the average frequency of the average multiplet increases linearly with the atomic number with the exception of the case where $x=0$.

In a similar manner, we can compare the lines of the elements beginning with Al. The transitions to be compared in this case will be $xM_2 (N_1 \leftarrow N_2)$, x varying from 0 to 6.

TABLE II.

$x \rightarrow$	0	1	2	3	4	5	6
I	Al	Si	P	S	Cl	A	K
II	Si ⁺	P ⁺	S ⁺	Cl ⁺	A ⁺	K ⁺	Ca ⁺
III	P ⁺⁺	S ⁺⁺	Cl ⁺⁺	A ⁺⁺	K ⁺⁺	Ca ⁺⁺	Sc ⁺⁺

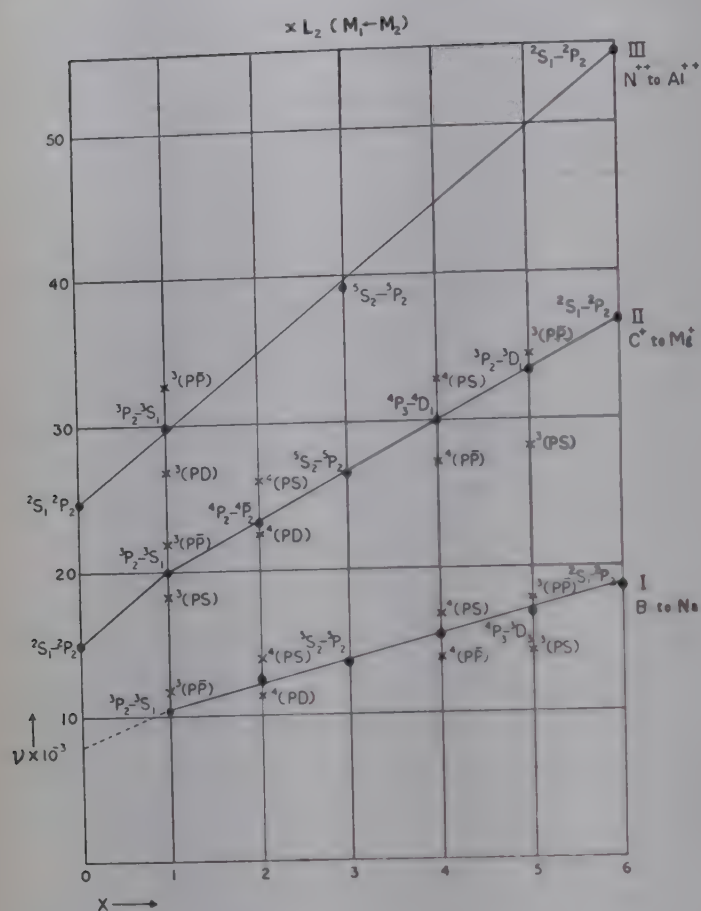


FIG. 1

The elements are shown in Table II and their respective lines are given in Chart II. The relations between the frequencies and the atomic numbers in the three types of spectra are illustrated graphically in fig. 2. That the relations are linear in this case also (with the exception where $x=0$) is clear.

For comparison, the positions of multiplets other than the average multiplets (for which only the relation is linear) are indicated by a cross (×) in the figures 1 and 2. They show by how much these multiplets differ from the normal relations.

It is now apparent that location of spectra of elements, in such a group as we have considered, can be made, provided we know the spectra of two or more elements in the group. In fact, as already has been mentioned, this method of location has been used with advantage in the classification of a number of elements. The applicability of this method, in addition to that of the irregular doublet law, was shown in the spectrum of ionised sodium², which was treated as the mean between the spectra of Ne⁺ and Mg⁺. Where irregular doublet law is not applicable for want of data, this method of location is of special importance. Recently Mr. D. K.

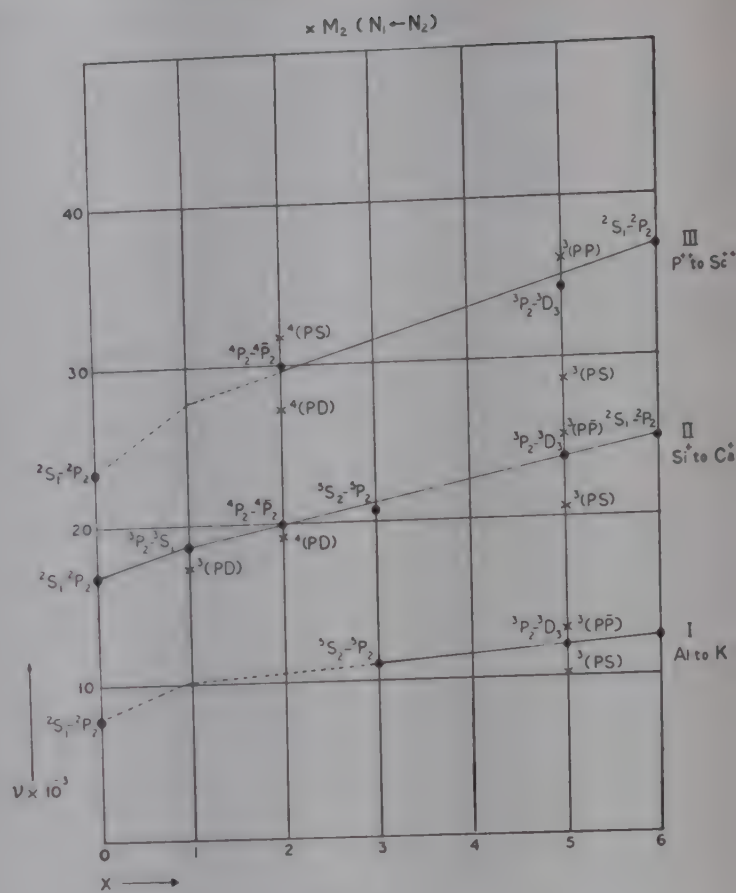


FIG. 2

Bhattacharyya has applied this method of location in the spectra of ionised sulphur and of doubly ionised sulphur with some amount of success.

This method, though not so accurate as the irregular doublet law, has one advantage over it, inasmuch as the successive changes in the frequencies (ν) when we pass on from one element to another is much smaller than when we apply the irregular doublet law. In the latter case the changes are sometimes as great as, or even more than, the frequency of the first member in the group. As for example, in passing from C to N⁺ the $\nu=9468$ (in C, $\nu=10348$) whereas in passing from C to N, the change is only 1827 (*vide* Chart I). Therefore, if we know the spectrum of only one member, the preceding or the succeeding, in a group, we can approximately locate the position of the spectrum of an element, since the change is not great. By this means, knowing the spectrum of Sc⁺⁺, that of Ca⁺⁺ was located and analysed. The details of the results will be published separately.

The correctness of the above-mentioned results enables us to predict with confidence the lines in the spectra of elements which remain to be classified. These have been shown in brackets [] in Charts I and II.

The theoretical aspects of these considerations are in progress and will it is hoped, form the subject of a subsequent paper.

²Majumdar, *Ind. Jour. Phys.*, 2, 348 (1928)

CHART II

$$xM_2 (N_1 \leftarrow N_2)$$

$x \rightarrow$	0	1	2	3	4	5	6
(1)	..	$^3P_2 - ^3D_2$	$^4P_2 - ^4D_2$	..	$^4P_2 - ^4P_2$	$^3P_1 - ^3S_1$	..
(2)	$^2S_1 - ^2P_2$	$^3P_2 - ^3S_1$	$^4P_2 - ^4P_2$	$^5S_2 - ^5P_2$	$^4P_2 - ^4D_2$	$^3P_2 - ^3D_2$	$^2S_1 - ^2P_2$
(3)	..	$^3P_2 - ^3P_2$	$^4P_2 - ^4S_2$		$^4P_2 - ^4S_2$	$^3P_1 - ^3P_2$	
I	Al	Si	P	S	Cl	A	K
(1)	..	..	..	..	..	10351	..
(2)	7617	[9700]	[10300]	11044	11937	12318	13043
(3)	..	..	..	..	..	13380	..
	Fowler, Report, p. 156.			Fowler, Report, p. 170.	K. Majumdar (unpublished)	Meissner, Zs. f. Phys. 40, 839 (1927).	Fowler, Report, p. 120.
II	Si ⁺	P ⁺	S ⁺	Cl ⁺	A ⁺	K ⁺	Ca ⁺
(1)	..	16453	18144	..	..	20701	..
(2)	15751	18877	20026	20784	..	23881	25414
(3)	..	18425	21197	..	..	24917	..
	Fowler, Phil. Trans. 225, 24 (1926).	Bowen Phys. Rev. 29, 511 (1927).	Bhatta- charyya, Nature, (Communi- cated).	Paschen Annd. Phys. 71, 560 (1923).		Bowen, Phy. Rev. 31, 497 (1928).	Fowler, Report, p. 127.
III	P ⁺⁺	S ⁺⁺	Cl ⁺⁺	A ⁺⁺	K ⁺⁺	Ca ⁺⁺	Sc ⁺⁺
(1)	..	..	27238	..	..	28258	..
(2)	23678	..	30030	[31200]	[33100]	34475	37039
(3)	..	..	31845	..	..	35811	..
	Millikan & Bowen Phy. Rev. 25, 601, (1925).		Bowen, Phy. Rev. 31, 35 (1928).		Bowen, do.	Bowen, do. Majumdar and Toshniwal, Nature.	Russell, Astro. Journ. 66, 13 (1927).

47. ON NEW METHODS IN STATISTICAL MECHANICS*

M. N. SAHA AND R. C. MAJUMDAR

(*Phil. Mag., Sr. VII, 9, 584, 1930*)

At the present time a number of new methods are being developed in statistical mechanics, and it is difficult to see the connexion amongst them. In this essay an attempt is made to review these methods and supply the link amongst the different theories.

Almost all the old (Planck) and new methods (Bose-Einstein⁽¹⁾, Fermi-Dirac⁽²⁾) start with Boltzmann's theorem

$$S = k \log W,$$

and with Planck's definition of W , viz.:—

$W = \text{Thermodynamical Probability.}$

There is an alternative function G due to Boltzmann⁽³⁾ and Gibbs⁽⁴⁾ which may be described as the total phase volume described by a thermodynamical system. Ehrenfest and Trkal⁽⁵⁾ treat problems of chemical equilibrium etc. with the aid of this function (they called it $\{\gamma\}$), and find their method superior to Planck's. There is a certain amount of ambiguity in Planck's definition of W ; according to him W is a whole number, but Ehrenfest and Trkal have shown that Planck's expression for W has to be divided by $N!$ to get the correct expression for S . The need for this operation is not clear. Planck⁽⁶⁾ has apparently admitted the soundness of this criticism, and in a recent paper puts a new interpretation on W . He defines W as the maximum number of probable states which can give rise to the total energy E . Planck shows that, with this definition,

$$W = \frac{G}{h^{3N} N!} \quad (1)$$

The same conclusion has been reached independently and simultaneously by Saha and Sur⁽⁷⁾ from different conceptions. They emphasize the necessity for laying down a unit of probability. At absolute zero $S=0$ and $W=1$, and the total phase-volume described $= h^{3N} N!$ in the simplest case (*i.e.*, a perfect monatomic gas). Denoting this by G_0 , and the corresponding probability by unity, the mathematical value of probability at any temperature

$$W = \frac{G}{G_0} = \frac{G}{h^{3N} N!}.$$

The conceptions of Planck and Saha and Sur, though apparently different, are in essence identical.

We shall therefore start with the theorem (1) and calculate W , introducing (1) classical conceptions, (2) the Fermi-Dirac condition, (3) the Bose-Einstein condition.

Let us suppose the assembly to be distributed in energy layers with the energy-interval $(\epsilon_s, \epsilon_s + d\epsilon_s)$ for each particle, and let N_s be the number of particles in this interval. The phase-volume occupied by each particle

$$g_s = 2\pi V (2m)^{3/2} \epsilon_s^{1/2} d\epsilon_s. \quad (2)$$

Then, according to Ehrenfest and Trkal,

$$G = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s}. \quad (3)$$

This theorem has been given by Ehrenfest and Trkal without proof, though to many it may not be so self-evident. We are therefore supplying a proof. Let G_N denote the phase-space described by N -particles, and G_{N-1} the phase-space described by $N-1$ -particles, the remaining particle being assigned to the region $(dx dy dz dp_x dp_y dp_z)$. We have

$$G_N = \frac{V^N (2\pi m)^{\frac{3N}{2}} E^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2} + 1\right)} \quad (3')$$

Now we have⁽⁸⁾

$$\frac{G_{N-1}}{G_N} = \frac{dw}{d\tau} \quad (4)$$

where dw is the probability that the particle is to be found in the phase-volume considered. We have therefore

$$dw = \frac{N_s}{N},$$

and $d\tau$ the phase-volume of the particle under question $= g_s$. Thus

$$G_N = G_{N-1} \cdot \frac{g_s}{(N/N)}$$

Then by successive application of the same theorem

$$G_N = G_{N-N_s} \left(N \frac{g_s}{N_s} \right)^{N_s},$$

and finally, taking all the energy-layers,

$$G_N = \prod_s g_s^{N_s} \left(\frac{N}{N_s} \right)^{N_s} = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s} \quad (3)$$

We have thus reduced the calculation of the phase-volume from the $6N$ dimensional space to one of 6

* Communicated by the Authors.

dimensions. We shall now show that the classical expression for entropy is easily obtained from this value of G . We have

$$W = \frac{1}{\prod N_s!} \prod_s \left(\frac{g_s}{h^3} \right)^{N_s}.$$

Let $\frac{g_s}{h^3}$ be denoted by a_s ;

then $S = k \log W$

$$= k \left\{ \sum_s N_s \log a_s - \sum_s N_s (\log N_s - 1) \right\}$$

$$= k \sum_s N_s \log \frac{a_s}{N_s} + kN. \quad (4)$$

Now

$$\left. \begin{aligned} E &= \sum_s N_s \epsilon_s \\ N &= \sum_s N_s \end{aligned} \right\} \quad (5)$$

Hence, applying the variation-principle,

$$\left. \begin{aligned} \delta S &= \sum_s \delta N_s (\log a_s - \log N_s) \\ \delta N &= \sum_s \delta N_s \\ \delta E &= \sum_s \delta N_s \epsilon_s \end{aligned} \right\} \quad (6)$$

Therefore $\log a - \log N + \lambda \epsilon_s + \mu = 0$

or $N_s = a a_s e^{\beta \epsilon_s} \quad (7)$

It can now be easily proved in the usual way that

$$\beta = -\frac{1}{kT}, \quad \text{and} \quad \frac{1}{\alpha} = \frac{V}{N h^3} (2\pi m k T)^{3/2} \quad (8)$$

and substituting these values, we can easily show that S gets the classical value, viz.,

$$Nk \log \left\{ \frac{V}{N h^3} (2\pi m k T)^{3/2} e^{5/2} \right\} \quad (9)$$

Now we shall show how the Fermi-Dirac expression can be obtained from the definition of W .

The phase-volume of the assembly

$$G = \frac{N!}{\prod N_s!} \prod_s g_s^{N_s}$$

has been calculated on the supposition that the phase-volume occupied by each individual particle is infinitely small compared with the total phase-volume at its disposal, viz., g_s . Let us now give up this assumption, and suppose it occupies a finite phase-volume " a ". Then

$$G = \frac{N!}{\prod N_s!} \prod_s g_s (g_s - a) \dots (g_s - \overline{N_s - 1} a). \quad (10)$$

The argument is just the same as that which we introduce in the calculation of the van der Waals's correction " b " from probability consideration. When each particle occupies negligible volume we have

$$W \propto V^N;$$

but when the volume " β " cannot be neglected,

$$W \propto \prod_{\gamma=1}^N (V - \gamma - 1 \beta).$$

In the above method we have introduced the phase-volume g_s instead of the space-volume V , and calculated G_N . Now

$$W = \frac{G}{h^{3N} N!}$$

$$= \frac{1}{\prod N_s!} \prod_s \left(\frac{g_s}{h^3} \right) \dots \left(\frac{g_s}{h^3} - \overline{N_s - 1} a \right)$$

$$= \frac{1}{\prod N_s!} \prod_s a_s (a_s - \epsilon) \dots (a_s - \epsilon \cdot \overline{N_s - 1}),$$

where

$$\epsilon = \frac{a}{h^3},$$

$$= \prod_s \frac{a_s!}{N_s! (a_s - \epsilon N_s)!} \quad (11)$$

If we put $\epsilon = 1$, we get the Fermi-Dirac expression for W ; when $\epsilon = -1$ we have

$$W = \prod_s \frac{a_s + \overline{N_s - 1}!}{(a_s - 1)! N_s!}, \quad (12)$$

which is the Bose-Einstein expression for W .

It may be mentioned here that the above discussion was originally inspired by an article of L. Brillouin (*Ann. d. Phys.* vii. 1927). But in spite of apparent resemblance, the method given here differs in essential points from Brillouin's. Firstly, Brillouin follows Bose-Einstein and Fermi-Dirac closely in calculating probability by making use of a_s (which is Brillouin's g_s) as the number of degrees of freedom which a particle can have when its energy lies between ϵ_s and $\epsilon_s + d\epsilon_s$. It may be easily shown that though we obtain the various values of N_s by subjecting Brillouin's expressions for W to the usual variational process in the three different cases (equations 21), they do not give us absolute values of entropy unless some assumption is made regarding the value of A or G in equation (21) of Brillouin. We have to make $\frac{G}{a} = N$ in order to get the correct value of S . The justification

for this assumption is not clear, and Brillouin has made no attempt to calculate the absolute value of S . He devotes a good deal of discussion over the origin of the permutability factors $\frac{N!}{\prod N_s!}$, which is quite unnecessary. The factor comes out automatically when we calculate the total phase-volume of the ensemble not in $6N$ dimensions, but in 6 dimensions.

The above method has therefore the merit of giving a deduction for the absolute value of S on the three views from a unitary standpoint. The classical statistics and Fermi-statistics are easily understandable, and probably in the case of Fermi-Dirac statistics it affords a clearer physical view of the case than Fermi's original method. There may be many who share with us the difficulty in understanding

the extension of the Pauli Principle, which has been shown to be the guiding principle in the formation of atoms out of protons and electrons, to the case of an ensemble of N independent particles possessing only translatory motion (e. g., Hall, Proc. Nat. Acad. Sci. 1928). The deduction given here follows exactly the same lines as the deduction of the van der Waals's correction for finite volumes, and is therefore physically more comprehensible.

Of greater difficulty is the comprehension of the Bose-Einstein statistics. Here " a ", the phase-volume of any particle, has to be put negative ($-h^3$). These statistics have therefore to be definitely ruled out in the case of material particles. But as it is found to be correct in the statistics of light-particles, we have to assume that when a photon enters a phase-space, the space expands, since the total

phase-volume is increased by the phase-volume of the photon. A discussion will be found in Brillouin's paper above referred to.

References

- (1) Bose, *Zeits. f. phys.* xxvii. p. 384 (1924). Einstein, *Sitz. Preuss. Akad.* p. 261 (1924); p. 3 (1925).
- (2) Fermi, *Zeits. f. phys.* xxxvi. p. 902 (1926). Dirac, *Proc. Roy. Soc. A*, cxii. p. 66, (1926).
- (3) Boltzmann, "Über die Eigenschaften Monozyklischer System" *Wien. Ber.* xc. (1884); *Wiss. Abhandl.* iii. Nr. 73. S. 132ff.
- (4) Gibbs, 'Statistical Mechanics.'
- (5) Ehrenfest and Trkal, *Proc. Amst. Acad.* xxiii. (1920).
- (6) Planck, *Zeits. f. phys.* xxxv. p. 155 (1925).
- (7) Saha and Sur, *Phil. Mag.* i. p. 280 (1926).
- (8) Jeans, 'Dynamical Theory of Gases,' 2nd ed. chap. iv. pp. 58-62. Wassmuth, *Statistische Mechanik.*

48. COLOURS OF INORGANIC SALT

(*Nature*, **125**, 163, 1930)

No satisfactory explanation of the colours of inorganic salts in the vapour state, in solution, or in crystalline form has yet been put forward, excepting certain suggestions by Fajans ("Handbuch der Physik", Bd. 24, p. 564), that the colours are due to the deformation of the cation produced by surrounding anions and molecular complexes. The ideas of Fajans were rather vague, but the time has now come to put forward a more precise hypothesis. It is well known that salts like NaCl, CaCl₂, AlCl₃ in which the electrons of the cation form closed shells (p^6), are colourless or white. Herzfeld found from a study of dispersion of NaCl that there are three ultra-violet absorption bands, one at $\lambda 340$ which was ascribed to Na⁺, another at about $\lambda 1500$, which was ascribed to Cl⁻ ion. This last one has been experimentally obtained by Pfund (*Phys. Rev.*, vol. 32) by the *Reststrahlen* method. The wave-length $\lambda 340$ ascribed to Na⁺ agrees remarkably well with the resonance line of Na⁺ identified by K. Majumdar (*Ind. Jour. Phys.*, 1927) and Bowen, though definite assignment of values of the absorption wave-length from dispersion data in this region is subject to certain uncertainties.

Colours are almost entirely shown by the compounds of the transitional group of elements (the first group consisting of elements from scandium to copper). Let us fix our attention on the first group alone, as the same arguments will apply to other groups. The colours are somewhat modified by the anion, or the state of aggregation (solution or crystal), but intrinsically it is due to the cation. Taking a compound like CrCl₃, we can say that it consists of a Cr⁺⁺⁺-ion, surrounded by three Cl⁻ ions. The absorption of light in the visible region is due entirely to the outer

electrons of the Cr⁺⁺⁺-ion. Let us see how this absorption takes place.

The outermost shell of the Cr⁺⁺⁺-ion (and generally of all ions of transitional elements) consists of a number of electrons in the d -shell. In Cr⁺⁺⁺, the number is 3. The multiplicity of the most stable combination state is obtained by adding up the multiplicity vector $r = \frac{1}{2}$ for all the electrons, and the next metastable states are obtained by reversing the vector r for one of the electrons. In d^3 , the states are respectively 4X and 3T , where X and T are further to be formulated. This is obtained by considering the l -coupling according to Pauli's principle, and in the case of Cr⁺⁺⁺, $X = F$ and P in 4X , and $T = H, G, D$ in 3T . The average difference in energy between the terms obtained in this way, that is, by having the rotating quantum number all in one direction, and then reversing only one, is about $C_{av} = 20,000$, the value increasing with the number of net charges in the nucleus, as shown by the spectroscopic data of Russell, Gibbs and White, Lang, Shenstone, etc. (see various papers in the *Physical Review*).

It is therefore evident that the absorption of light in the visible region is due to some of the d -electrons changing their r -vector from $\frac{1}{2}$ to $-\frac{1}{2}$. This type of transition is possible only in transitional groups, and though usually forbidden they become very prominent in all molecular formations. We cannot, of course, expect that the values of energy difference which we obtain from spectroscopic studies will continue to hold good in molecules or complex formation, but they will remain of the same order of magnitude. An indefiniteness will be introduced by the modification of the rules of l -coupling (*vide* Stoner's

suggestive paper in the *Phil. Mag.*, September 1929, which explains D. M. Bose's hypothesis that it is only the rotating vector τ which is responsible for the magnetism of the ions of transitional elements in a similar way).

There seems to be no experimental evidence in existence which can be utilised in support of the above hypothesis. The absorption spectra of none of these compounds have been studied in the vapour state (the work of Franck and his school being confined mostly to the study of alkali

halogenides). The emission spectra of some of these salts have been studied, but it is difficult to draw any conclusion from them. Other interesting experiments may also be devised to test the above hypothesis. Some of them are in progress.

Department of Physics,
Allahabad University,
Dec. 27, 1929.

49. ÜBER DIE VERTEILUNG DER INTENSITÄT UNTER DIE FEINSTRUKTUR-KOMPONENTEN DER SERIENLINIEN DES WASSERSTOFFS UND DES IONISIERTEN HELIUMS NACH DER DIRACSCHEN ELEKTRONENTHEORIE.

Von M. SAHA und A. C. BANERJI

(*Zeits. f. Physik*, **63**, 704, 1931)

Mit 4 Abbildungen. (Eingegangen am 5. Oktober 1930)

1. *Einleitung.* Die Feinstruktur der Linien des Wasserstoffs und ionisierten Heliums sowie die Intensitätsverteilung unter die Feinstrukturkomponenten sind in älterer und neuester Zeit Gegenstand der Untersuchungen vieler hervorragender Forscher gewesen¹. Auch heute ist das Interesse daran noch nicht erloschen, da L. Goldstein in einer vor kurzem im *Journal de Physique* (Dezember 1929) erschienenen Arbeit die Intensitätsverteilung unter die Feinstrukturkomponenten von H_α und $\lambda=4686$ des He^+ nach der relativistischen Wellenmechanik von Dirac untersuchte und recht auffallende Abweichungen gegenüber den Beobachtungen fand. Das Ergebnis schien aus zwei Gründen einigermaßen überraschend: 1. ist die Diracsche Elektronentheorie so erfolgreich in der Deutung der Dublizität und der Feinstruktur der H-Linien gewesen, dass an ihr Versagen in der Intensitätsberechnung nur schwer zu glauben ist, und 2. haben Sommerfeld und Unsöld in der oben genannten Arbeit eine Theorie der Intensitätsverteilung auf Grund von Schrödingermechanik und statistischen Überlegungen ausgearbeitet, mit deren Hilfe sie in sehr befriedigender Form viele der voneinander abweichenden Beobachtungen der Intensitätsverteilung auf die Feinstrukturkomponenten der H_α -Linie und von $\lambda=4686$ des He^+ erklären konnten. Die Verfasser der vorliegenden Arbeit sind mit dieser selben Frage schon vor der Veröffentlichung der Goldsteinschen Arbeit beschäftigt gewesen, aber ihre Ergebnisse stehen mit den

Versuchsergebnissen in ausgezeichnete Übereinstimmung, ebenso wie mit den Ergebnissen von Sommerfeld und Unsöld. Wir haben die Diracsche Theorie in der von Weyl und Darwin² gegebenen Form benutzt. Die vorliegende Arbeit enthält nur die Endergebnisse, da die Wiedergabe aller mathematischen Schritte zu umfangreich und langweilig werden dürfte.

2. *Historische Skizze der Frage.* Die Theorie für die Feinstruktur der H-Linien ist bekanntlich zuerst von Sommerfeld auf Grund der Elektronenniveautheorie ausgearbeitet worden. Ist ein Elektronenniveau durch die Gesamtquantenzahl n und die azimutale Quantenzahl k gegeben, so ist seine Energie durch

$$\nu_{nk} = -Rz^2 \left[\frac{1}{n^2} + \frac{\alpha^2}{n^4} \left(\frac{n}{k} - \frac{3}{4} \right) \dots \right] \quad (1)$$

ausgedrückt. (Die Energie des Niveaus ist gleich $h\nu_{nk}$. α ist die Sommerfeldsche Feinstrukturkonstante $\left(\frac{2\pi e^2}{ch} \right)$. Die Frequenz einer Emissionslinie ist durch

$$\nu = Rz^2 \left[\frac{1}{n^2} - \frac{1}{n'^2} \right] + R\alpha^2 z^2 \left[\frac{1}{n^4} \left(\frac{n}{k} - \frac{3}{4} \right) - \frac{1}{n'^4} \left(\frac{n'}{k'} - \frac{3}{4} \right) \right] = \nu_0 + \Delta\nu \quad (2)$$

gegeben, wo

$$\left. \begin{aligned} \nu_0 &= Rz^2 \left[\frac{1}{n^2} - \frac{1}{n'^2} \right] \\ \Delta\nu &= R\alpha^2 z^2 \left[\frac{1}{n^4} \left(\frac{n}{k} - \frac{3}{4} \right) - \frac{1}{n'^4} \left(\frac{n'}{k'} - \frac{3}{4} \right) \right] \end{aligned} \right\} 2)$$

¹Für einen zusammenfassenden Bericht vgl. A. Sommerfeld, *Atombau und Spektralanalyse*, 4. Aufl., S. 439 ff. Die dort vertretenen Ansichten sind inzwischen abgeändert worden; vgl. A. Sommerfeld u. A. Unsöld, *Zeit. f. Phys.* **36**, 259, 1926; **38**, 237, 1926.

²H. Weyl, *Gruppentheorie und Quantenmechanik*, Kap. 4, S. 1
C. G. Darwin, *Proc. Roy. Soc. (A)* **118**, 654, 1928.

Die Feinstrukturkomponenten erhält man, indem man k und k' alle möglichen Werte verleiht und im jede Kombination $\Delta \nu$ ausrechnet. Im folgenden geben wir die Komponenten für H_α wieder:

$$\begin{array}{ll}
 \text{a) } 2P_{3/2} & 2_2 \leftarrow 3_3 \quad 3D_{5/2} \quad \text{(I)} \\
 \text{b) } 2P_{1/2} & 2_1 \leftarrow 3_2 \quad 3D_{3/2} \quad \text{(II)} \\
 & 2S_{1/2} \quad 3P_{3/2} \\
 & \quad \quad 3_1 \quad 3P_{1/2} \quad \text{(III)} \\
 & \quad \quad 3S_{1/2}
 \end{array}$$

Jedoch zeigte Landé-später, dass die Feinstruktur in Wirklichkeit nicht relativistischen, sondern magnetischen Ursprungs ist, d.h. dass sie darauf beruht, dass das Elektron ein magnetisches Moment besitzt. Nach der Landéschen Theorie, die Sommerfeld und Unsöld³ übernommen und durch die von Goudsmit und Uhlenbeck stammende Annahme rotierender Elektronen auf eine anschaulichere Grundlage gestellt haben, ist der Bau des H-Spektrums genau analog dem der Alkalispektren. Heisenberg und Jordan⁴ haben der Hypothese die strenge mathematische Fundierung gegeben sie zeigten vermittelt der Matrizenmechanik, dass sich für solche Glieder wie 3_{32} und 3_{33} (d.h. $3D_{3/2}$ und $3P_{3/2}$), die dieselbe innere Quantenzahl besitzen, derselbe Energiewert wie für den Sommerfeldschen 3_s -Term ergibt. Die auf dieser Grundlage berechnete Struktur gibt die Fig. 1 für H_α in der Bezeichnung von Russell und Saunders wieder.

In der ersten Spalte sind die Niveaus nach dem Russell-Saunderschen Schema mit ihren inneren Quantenzahlen bezeichnet. Die zweite Spalte enthält die Diracschen k -Werte für jeden Term. Die dritte Spalte gibt die Schrödingerschen l -Werte. In der vierten Spalte findet sich die

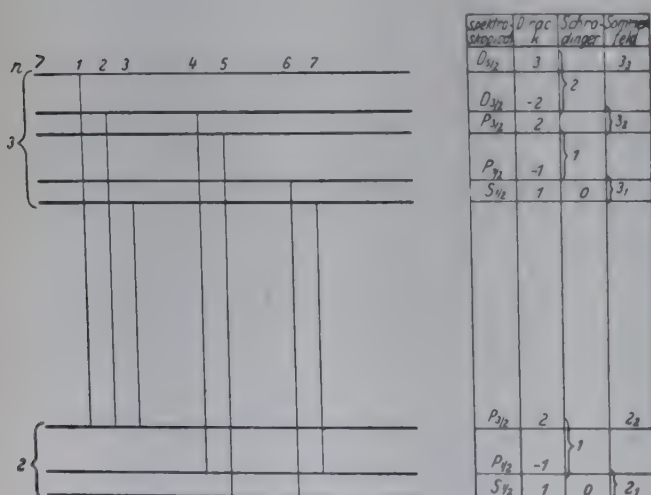


FIG. 1

ursprüngliche Sommerfeldsche Zuordnung. $D_{3/2}$ und $P_{3/2}$ haben denselben Energiewert wie das Sommerfeldsche 3_2 , entsprechend $P_{1/2}$ und $S_{1/2}$ denselben wie 3_1 .

Im Gegensatz zum ursprünglichen Sommerfeldschen Schema besteht die H_α -Linie nunmehr aus sieben anstatt wie bei Sommerfeld aus drei Komponenten; da aber die Energiewerte von $D_{3/2}$ und $P_{3/2}$ sowie von $P_{1/2}$ und $S_{1/2}$ zusammenfallen, so fallen auch einige der Komponenten aufeinander. So fällt zusammen

- Ia mit (1)
- IIa „ (2)
- (nach Sommerfeld verboten)
- IIIa mit (3)
- IIb „ (4, 5)
- IIIb „ (6, 7)

Lage und beobachtete Intensität dieser Linien auf einer Frequenzskala zeigt die Fig. 2.

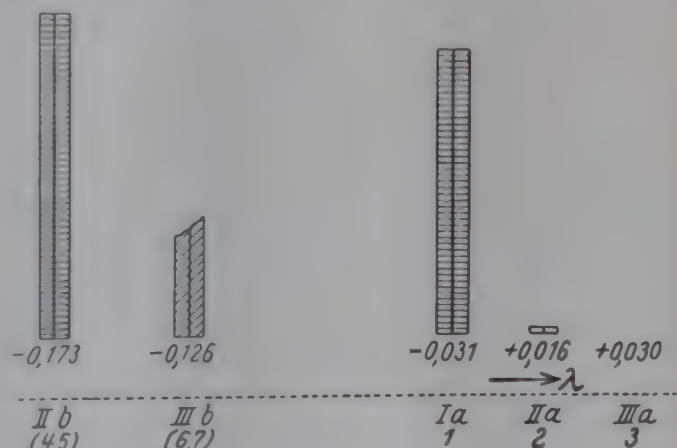


FIG. 2

Komponenten von H_α
Abszisse: Wellenlänge. Ordinate: Intensität
Die Komponenten sind an den ihnen zugehörigen Wellenlängen eingezeichnet.

In Wirklichkeit können im Versuch nur die rote (1) und die violette Komponente (4, 5) deutlich unterschieden werden.

Es ist klar, dass die Intensitäten der Komponenten, die irgend einem Multiplett zugeordnet werden können, die Intensitätsformel von Ornstein-Burger-Sommerfeld befriedigen müssen. Wir stellen daher die Komponenten von H_α in der Form der Multipletts dar, aus denen diese Linie zusammengesetzt ist (Fig. 3).

Man sieht, dass die H_α -Linie aus drei Multipletts besteht: 1. einem $2P-3D$ -Multiplett, das aus den Linien (1, 2, 4) besteht, die in kleinen Zahlen in den oberen rechten Ecken jedes Quadrats angegeben sind. Ihre Intensitäten sollten sich wie 9:1:5 verhalten; 2. einem $2S-3P$ -Multiplett, bestehend aus den Linien (5, 6); das Intensitätsverhältnis sollte 2:1 betragen; 3. einem $2P-3S$ -Multiplett, das aus den Linien (3, 7) besteht. Das Intensitätsverhältnis sollte 2:1 sein.

³A. Sommerfeld u. A. Unsöld, *Zeit. f. Phys.* **36**, 259, 1926.

⁴W. Heisenberg u. P. Jordan. *ebenda*, **37**, 263, 1926.

	1	-1	2	-2	3
2	$S_{1/2}$	$P_{1/2}$	$P_{3/2}$	$D_{3/2}$	$D_{5/2}$
1	$S_{1/2}$	1 $\begin{smallmatrix} 6 \\ 0,110 \end{smallmatrix}$	2 $\begin{smallmatrix} 5 \\ 0,031 \end{smallmatrix}$		
-1	$P_{1/2}$	1 $\begin{smallmatrix} 7 \\ 0,110 \end{smallmatrix}$		5 $\begin{smallmatrix} 4 \\ 0,031 \end{smallmatrix}$	
2	$P_{3/2}$	2 $\begin{smallmatrix} 3 \\ 0,031 \end{smallmatrix}$		1 $\begin{smallmatrix} 2 \\ 0,021 \end{smallmatrix}$	9 $\begin{smallmatrix} 1 \\ 0,005 \end{smallmatrix}$

FIG. 3

Darstellung von H_a als Kombination dreier Multipletts.

Zum Vergleich von Versuchsdaten mit irgendwelchen theoretischen Ergebnissen müssen wir das Verhältnis der Intensitätseinheiten in den drei Multipletts kennen. Wir können diese Einheiten als I_{2P-3D} , I_{2S-3P} und I_{2P-3S} definieren. Zum Beispiel besteht die rote Komponente von H_a praktisch aus (1) des $2P-3D$ -Multipletts, während die violette Komponente aus (4) von $2P-3D$ und (5) von $2S-3P$ zusammengesetzt ist. Daher ist $I_{\text{violett}}/I_{\text{rot}} = (5 I_{2P-3D} + I_{2S-3P})/9 I_{2P-3D}$. Ohne I_{2S-3P}/I_{2P-3D} zu erkennen, können wir keinen Vergleich anstellen.

Die kleinen Zahlen (0,005, 0,020 usw.) geben die von Goldstein gefundenen relativen Intensitäten. Ein Blick auf die Tabelle zeigt, dass die Abweichung von den Versuchsergebnissen recht krass ist. Die Komponente (1) wird hier zur schwächsten, während sie die stärkste sein sollte, und die Regel von Ornstein-Burger-Sommerfeld ist gröblich verletzt.

Das Vorgehen von Sommerfeld und Unsöld⁵. Dagegen finden Sommerfeld und Unsöld von der Schrödingerschen Form der Wellenmechanik und von statistischen Überlegungen ausgehend, gute Übereinstimmung mit den Hansenschen⁶ Ergebnissen für H_a und Paschens⁷ neuen Messungen an $\lambda=4686$. Sie benutzen die Schrödingersche Mechanik, die, wenn sie auch das Dublizitätsphänomen nicht zu erklären vermag, doch einen Grenzfall der Diracschen Gleichungen für $c \rightarrow \infty$ darstellt. Es ergibt sich, dass jedes der drei Multipletts $I_{2P-3D} : I_{2S-3P} : I_{2P-3S}$, aus denen H_a zusammengesetzt ist, als eine einfache Linie angeselen wird, und die Gesamtenergie wird genau durch das benutzte Verfahren gegeben. Sie finden

$$\text{Gesamtintensität von } 2P-3D : 2S-3P : 2P-3S \\ 1 : 5/24 : 5/2^8$$

Nun verhalten sich die statistischen Gewichte der drei Multipletts wie 15:3:3. Daher verhalten sich die Intensitätseinheiten der drei Multipletts wie $1/15 : \frac{5}{24 \cdot 3} : \frac{5}{2^8 \cdot 3}$ oder wie 1:1,04:0,09.

Somit ist die Intensität der roten Komponente gleich 9, die violetten Komponente gleich $5I_{PD} + 2I_{SP} = 7,08$.

Für die $H\epsilon$ -Linie $\lambda=4686$ gehen Sommerfeld und Unsöld ganz analogen Weg und kommen zu Ergebnissen, die sich in guter einstimmung mit Beobachtungsdaten erwiesen haben.

Verfahren dieser Arbeit. Wie wir schon oben erwähnten, sind wir direkt von der Diracschen Elektronentheorie in der Darwin-Weylschen Darstellung ausgegangen und haben die Übergangswahrscheinlichkeiten z , $x+iy$, $x-iy$ für jede Feinstrukturkomponente abgeleitet. Das Verfahren liefert Formeln, die die Intensitäten der magnetischen Komponenten jeder Feinstrukturlinie wiedergeben, wie schon Heisenberg und Jordan⁸ und auch Dirac⁹ gefunden haben. Die Gesamtintensität jeder Feinstrukturlinie ist durch $\sum z^2 + \sum (x \pm iy)^2$ gegeben, wobei die Summation über die Eigenwerte von m erstreckt wird, was einfach $3\sum z^2$ gibt. Werden die Intensitäten der irgendein Multiplett (z. B. 1, 2, 4, die das $2P-3D$ -Multiplett bilden) bildenden Linien verglichen, so erhält man ihr Verhältnis genau in der von der Ornstein-Burger-Sommerfeldschen Regel geforderten Form (nämlich 9:1:5 im eben gegebenen Falle). Die Verhältnisse der Intensitätseinheiten werden berechnet und ergeben genau die von Sommerfeld und Ornstein berechneten Werte sowohl für H_a als auch für $\lambda=4686$.

3. Skizzierung der mathematischen Theorie. Wir sind im grossen ganzen der Methode und der Bezeichnungsweise von Weyl gefolgt, mit geringen Änderungen hier und dort. Die von Weyl für die ψ -Funktion gefundenen Ausdrücke können folgendermassen geschrieben werden:

$$\left. \begin{aligned} \psi_1 &= \frac{2V}{r} y_{k-1} - i \frac{W}{kr} y_k, & \psi_3 &= \frac{2V}{r} y_{k-1} + i \frac{W}{kr} y_k, \\ \psi_2 &= \frac{2(k-m-1)}{r} y_{k-1}^{m+1} + i \frac{(k+m+1)}{k} \frac{W}{kr} y_k^{m+1}, \\ \psi_4 &= \frac{2(k-m-1)}{r} y_{k-1}^{m+1} - i \frac{(k+m+1)}{kr} \frac{W}{kr} y_k^{m+1}, \end{aligned} \right\} (3)^{10}$$

ψ_3 ist zu ψ_1 , ψ_4 zu ψ_2 konjugiert. Hier ist

$$\left. \begin{aligned} y_k^m &= e^{im\phi} (\sin \Theta)^{-m} D^{k-m} (1-z^2)^k \\ D &= \left(\frac{d}{dz} \right), & z &= \cos \Theta \end{aligned} \right\} (4)$$

$$V = e^{-\beta r} F, \quad W = e^{-\beta r} G. \quad (5)$$

⁵W. Heisenberg u. P. Jordan, *Zeit. f. Phys.* **37**, 263, 1926.

⁶P.A.M. Dirac, *Proc. Roy. Soc. London (A)* **117**, 610, 1928.

¹⁰Diese Lösung unterscheidet sich von der ursprünglich von Darwin gegebenen und dann von Fraenkel (Wellenmechanik S. 284), Goldstein usw. wiedergegebenen in unwesentlichen Hinsichten, wovon man sich leicht durch einen Vergleich überzeugen kann.

⁵A. Sommerfeld u. A. Unsöld, I. c.

⁶G. Hansen, *Ann. d. Phys.* **78**, 558, 1925.

⁷F. Paschen, *ebenda*, **82**, 689, 1927.

F und G sind Polynome der Form:

$$\left. \begin{aligned} F &= r^{\mu_0} \sum_{s=0}^{s=n_r} a_{\mu_0+s} r^s, & G &= r^{\mu_0} \sum_{s=0}^{s=n_r} b_{\mu_0+s} r^s, \\ \mu_0 &= \sqrt{k^2 - \alpha^2}, & \alpha &= \frac{2\pi e^2}{ch} Z, \quad (\text{Sommerfeldsche Feinstrukturkonstante}) \\ \nu_0 &= \frac{m_0 c^2}{h}, & \sqrt{\nu_0^2 - \nu^2} &= \frac{1}{\alpha} [n_r + \sqrt{k^2 - \alpha^2}], \\ \beta &= \frac{\sqrt{\nu_0^2 - \nu^2}}{c} = \frac{z}{a(n_r + k)} = \frac{z}{an} \quad (\text{angenähert}). \end{aligned} \right\} (5')$$

n_r = radiale Quantenzahl,

n = Gesamtquantenzahl,

a = normaler Wasserstoffradius.

Für a_{μ_0+s} haben wir die folgenden Rekursionsformeln:

$$\left. \begin{aligned} a_{\mu_0+s+1} &= -a_{\mu_0+s} \cdot \frac{2(n_r-s)}{(s+1)(2k+s)} \cdot \frac{1}{an} \\ b_{\mu_0} &= a_{\mu_0} \frac{\alpha}{\mu_0 + k} \end{aligned} \right\} (6)$$

Daher sind G und infolgedessen W gegen V kleine Grössen; $|W|$ ist tatsächlich von der Grössenordnung $\alpha/|V|$.

Mit Hilfe der Rekursionsformeln für die Koeffizienten a können wir V in einer Form hinschreiben, die für manche Berechnungen brauchbarer ist:

$$V = a_0 Q^{\mu_0} e^{-\frac{\rho}{2}} L_{n+k-1}^{2k-1}(Q) \quad (7)$$

$$\text{mit} \quad Q = 2\beta r = \frac{2s}{n}, \quad s = \frac{r}{a}.$$

$L_{n+k-1}^{2k-1}(Q)$ ist das von Schrödinger eingeführte Laguerresche Polynom.

Die einzige unbekannte Konstante ist a_0 . Diese erhält man durch Normierung. Es sei

$$\lambda_{km} = \psi_1 \bar{\psi}_1 + \psi_2 \bar{\psi}_2 + \psi_3 \bar{\psi}_3 + \psi_4 \bar{\psi}_4, \quad (8)$$

dann müssen wir setzen:

$$\int \lambda_{km} d\Omega = 1, \quad (9)$$

Dies liefert uns den Wert für a_0 .

Lösungen für negative Diracsche k -Werte. Man kann leicht zeigen, dass

$$\left. \begin{aligned} \psi_1(-k) &= \frac{V}{kr} y_k^m - i \frac{2W}{r} y_{k-1}^m \\ \psi_2(-k) &= -\frac{V(k+m+1)}{kr} y_k^{m+1} - i \frac{2W}{r} (k-m-1) y_{k-1}^{m+1} \end{aligned} \right\} (10)$$

ψ_3 ist zu ψ_1 konjugiert und ψ_4 zu ψ_2 .

Da V die Gleichung

$$\frac{h^2}{8\pi^2 m} \left[\frac{d^2}{dr^2} - \frac{k(k-1)}{r^2} \right] V + UV = 0 \quad (11)$$

befriedigt, ist $V(-k) = V(k+1)$.

Die Normierung muss auf genau die gleiche Weise wie oben ausgeführt werden.

Übergangswahrscheinlichkeiten. Anfangs- und Endzustand seien durch die Zahlen (k, m) und (k', m') gegeben und ψ, ψ' seien die entsprechenden ψ -Funktionen. χ bedeute den Ausdruck

$$\chi = \psi_1 \bar{\psi}'_1 + \psi_2 \bar{\psi}'_2 + \psi_3 \bar{\psi}'_3 + \psi_4 \bar{\psi}'_4 \quad (12)$$

Wir wollen jetzt die mittleren Werte für die Verschiebungen

$z = r \cos \vartheta, \quad x + iy = r \sin \vartheta \cdot e^{i\varphi}, \quad x - iy = r \sin \vartheta \cdot e^{-i\varphi}$ berechnen. Dem Übergang $(k, m) \rightarrow (k', m')$ entsprechend haben wir

$$\left. \begin{aligned} \bar{z} &= \int r \cos \vartheta \chi d\Omega \\ \overline{x + iy} &= \int r \sin \vartheta e^{i\varphi} \chi d\Omega \\ \overline{x - iy} &= \int r \sin \vartheta e^{-i\varphi} \chi d\Omega \end{aligned} \right\} (13)$$

Jedes dieser Integrale lässt sich in der Form $R \cdot \Theta \cdot \Phi$ schreiben, wo R, Θ und Φ Integrale über r, ϑ bzw. φ allein bedeuten.

Es ist unnötig, die Schritte zu wiederholen, durch die bewiesen wird, dass

$$\left. \begin{aligned} \bar{z} \neq 0 &\text{ nur für } m' = m \\ \overline{x + iy} \neq 0 &\text{ „ „ } m' = m + 1 \\ \overline{x - iy} \neq 0 &\text{ „ „ } m' = m - 1. \end{aligned} \right\} (14)$$

Es ist dies das Auswahlprinzip für die magnetische Quantenzahl m .

Eine Betrachtung der Integrale Θ zeigt, dass Θ nur dann ungleich Null ist, wenn

$$k' = (k-1, k+1), (k-3, k+3), (k-5, k+5)$$

oder

$$k' = -k, -k \pm 2r \text{ usw.} \quad (15)$$

Dies Ergebnis entspricht dem Auswahlprinzip für die innere Quantenzahl $j = j+1, j-1, j$. In dieser Arbeit betrachten wir nur die Fälle

$$k = k+1, k-1, -k.$$

Das Integral $[R]$: In unseren Rechnungen haben wir meistens W vernachlässigt und $\mu_0 = \sqrt{k^2 - \alpha^2} = k$ gesetzt. Mit dieser Näherung erhalten wir

$$R = [r] = \frac{\int_0^\infty V(n, k) V(n', k') r dr}{\sqrt{\int_0^\infty V^2(n, k) dr \int_0^\infty V^2(n', k') dr}} \quad (16)$$

Der Wert für $[r]$ ist gegeben durch

$$[r] = \left\{ \frac{|n_r|}{(|n+k-1|)^3} \frac{|n_r|}{|n'+k'-1|} \right\}^{1/2} \frac{a \cdot 2^{k+k'}}{n^{k+1} n'^{k'+1}} \cdot S, \quad (16a)$$

wo S das von Sommerfeld¹¹ eingeführte Integral

$$S = \int_0^\infty e^{-\left(\frac{1}{n} + \frac{1}{n'}\right)s} L_{n+k-1}^{2k-1} \left(\frac{2s}{n}\right) L_{n'+k'-1}^{2k'-1} \left(\frac{2s}{n'}\right) s^{k+k'+1} ds \quad (17)$$

ist. Solange k und k' positiv sind, ergeben sich bei der Anwendung dieser Formeln keinerlei Schwierigkeiten. Wenn aber k negativ ist, treten einige Schwierigkeiten auf,

¹¹ Vgl. Wellenmechanischer Ergänzungsband S. 93.

wenn man eine allgemeine Formel hinschreiben will, Wir müssen dann $-k$ durch $k+1$ ersetzen; sicherer ist es aber, jeden Fall einzeln zu behandeln. Wir haben daher die Übergangswahrscheinlichkeiten für jeden der sechs Fälle $k \rightarrow k-1$, $k \rightarrow k+1$, $k \rightarrow -k \rightarrow -k+1$, $-k \rightarrow -k-1$, $-k \rightarrow k$ einzeln berechnet.

Die Werte für $\bar{z}$, $\overline{x+iy}$, $\overline{x-iy}$ sind für die verschiedenen $\ddot{U}$, gänge im folgenden zusammengestellt:

Die Faktoren $\sqrt{(k+m)(k-m-1)}$ usw. sind im wesentlichen mit den entsprechenden Ausdrücken in j und m identisch, die Heisenberg und Jordan¹² aus der Matrizenmechanik abgeleitet haben (vgl. Birtwhistle, New Quantum Theory, Kap XV, S. 122). Aber in den von Heisenberg und Jordan gefundenen Übergangswahrscheinlichkeiten ist $F_k^k \dots$ bezüglich der Koeffizienten B, C, A unbestimmt gelassen. Hier werden die F durch bekannte Größen dargestellt und berechnet.

Bezüglich der Ausdrücke für F kann die folgende erklärende Bemerkung von Nutzen sein.

n_r = radiale Quantenzahl im Sommerfeldschen Sinne. d. h. $n_r = n - k$, wenn die Diracsche k -Zahl $+k$ ist, und $n_r = n - (k+1)$, wenn die Diracsche k -Zahl $-k$ ist. So ist $k=2$ für $3 P_{3/2}$, hierfür ist $n_r=1$; $k=-1$ für $3 P_{1/2}$, auch hierfür ist $n_r=1$.

n' = Gesamtquantenzahl des Endzustandes (2 für H_α).

n'_r = radiale Quantenzahl des Endzustandes.

¹² W. Heisenberg u. P. Jordan, *Zeit. f. Phys.* **37**, 263, 1926.

Intensitätsberechnung. Die möglichen Werte der magnetischen Quantenzahl m sind

$$k-1, k-2, \dots, -k,$$

wenn die Diracsche Quantenzahl k oder $-k$ ist.

Die Ausdrücke für $\bar{z}$, $\overline{x+iy}$, $\overline{x-iy}$ setzen uns in den Stand, die Intensitäten der magnetischen Komponenten zu berechnen, in die irgendeine einzelne Linie aufspaltet, wenn sie in einem Magnetfeld angeregt wird: $\bar{z}$ entspricht der dem Felde parallel schwingenden Komponente, $\overline{x+iy}$ und $\overline{x-iy}$ beziehen sich auf die rechts und links zirkular polarisierten Komponenten.

Ohne Magnetfeld fallen alle diese Komponenten zu einer einzigen Linie zusammen. Für diesen Fall müssen wir die Summe der Intensitäten aller Komponenten berechnen. Man zeigt leicht, dass

$$\Sigma(\overline{x+iy})^2 = \Sigma(\overline{x-iy})^2 = 2\Sigma z^2.$$

Die Summation erstreckt sich in jedem einzelnen Falle über alle möglichen Werte von m . So haben wir für den Übergang $k \rightarrow k-1$ für $k=3$

$x+iy$, m durchläuft die Zahlen 2, 1, ... -1

oder $(k-1), k-2, \dots$

z , m durchläuft die Zahlen $(k-2) \dots$

$x-iy$, m „ „ „ $(k-3) \dots$

Die Gesamtintensität ist proportional

$$\begin{aligned} & \left\{ \frac{\Sigma(\overline{x+iy})^2 + \Sigma z^2}{\Sigma(\overline{x-iy})^2 + \Sigma z^2} \right\} \\ \text{oder} & \\ \text{oder} & = 3\Sigma z^2. \end{aligned} \quad (18)$$

Tabelle 1

Übergang	$\bar{z}$	$\overline{x+iy}$	$\overline{x-iy}$	F_k^k
$k \rightarrow k-1$	$\sqrt{(k+m)(k-m-1)}$	$\sqrt{(k-m-1)(k-m-2)}$	$\sqrt{(k+m)(k+m-1)}$	$\left\{ \left[\frac{ n_r }{(n+k-1)^3} \frac{ n'_r }{(n'+k-2)^3} \right]^{1/2} \frac{2^{2k-1}S}{n^{k+1}n'^k} \right\} \frac{a}{2k-1}$
$-k \rightarrow -k+1$	$\sqrt{(k+m)(k-m-1)}$	$\sqrt{(k-m-1)(k-m-2)}$	$\sqrt{(k+m)(k+m-1)}$	$\left\{ \left[\frac{ n_r }{(n+k)^3} \frac{ n'_r }{(n'+k-1)^3} \right]^{1/2} \frac{2^{2k+1}S}{n^{k+2}n'^{k+1}} \right\} \frac{a}{2k-1}$
$k \rightarrow k+1$	$\sqrt{(k-m)(k+m+1)}$	$\sqrt{(k+m+1)(k+m+2)}$	$\sqrt{(k-m)(k-m+1)}$	$\left\{ \left[\frac{ n_r }{(n+k-1)^3} \frac{ n'_r }{(n'+k)^3} \right]^{1/2} \frac{2^{2k+1}S}{n^{k+1}n'^{k+2}} \right\} \frac{a}{2k+1}$
$-k \rightarrow -k-1$	$\sqrt{(k-m)(k+m+1)}$	$\sqrt{(k+m+1)(k+m+2)}$	$\sqrt{(k-m)(k-m+1)}$	$\left\{ \left[\frac{ n_r }{(n+k)^3} \frac{ n'_r }{(n'+k+1)^3} \right]^{1/2} \frac{2^{2k+3}S}{n^{k+2}n'^{k+3}} \right\} \frac{a}{2k+1}$
$k \rightarrow -k$	$m + \frac{1}{2}$	$\sqrt{(k+m+1)(k-m-1)}$	$\sqrt{(k+m)(k-m)}$	$\left\{ \left[\frac{ n_r }{(n+k-1)^3} \frac{ n'_r }{(n'+k)^3} \right]^{1/2} \frac{2^{2+1}S}{n^{k+1}n'^{k+2}} \right\} \frac{a}{(2k-1)(2k+1)}$
$-k \rightarrow k$	$m + \frac{1}{2}$	$\sqrt{(k+m+1)(k-m-1)}$	$\sqrt{(k+m)(k-m)}$	$\left\{ \left[\frac{ n_r }{(n+k)^3} \frac{ n'_r }{(n'+k-1)^3} \right]^{1/2} \frac{2^{2k+1}S}{n^{k+2}n'^{k+1}} \right\} \frac{a}{(2k-1)(2k+1)}$

Daher ist die Intensität jeder Linie, sagen wir $k \rightarrow k-1$, durch den Ausdruck

$$\{F_k^{k-1}\}^2 \cdot f(k)$$

gegeben, wenn

$$f(k) = 3\Sigma(k+m)(k-m-1) \dots \text{usw.}$$

Es folgen die Werte für $f(k)$ für die verschiedenen Übergänge:

$$\left. \begin{aligned} & \left. \begin{aligned} k \rightarrow k-1 \\ -k \rightarrow -k+1 \end{aligned} \right\} \dots 2k(k-1)(2k-1), \\ & \left. \begin{aligned} k \rightarrow -k \\ -k \rightarrow k \end{aligned} \right\} \dots 2k(2k+1)(2k-1), \\ & \left. \begin{aligned} k \rightarrow k+1 \\ -k \rightarrow -k-1 \end{aligned} \right\} \dots 2k(k+1)(2k+1). \end{aligned} \right\} \quad (19)$$

Numerische Berechnung der Intensitäten. Zur Veranschaulichung schreiben wir die Intensitäten für die Komponenten (1, 4, 2), die das $2P-3D$ -Multiplett bilden, voll aus¹³:

$$I_1 = \left\{ \left[\frac{|n_r|}{(n+k-1)^3} \frac{|n'_r|}{(n'+k'-1)^3} \right]^{1/2} \frac{2^{2k-1}}{n^{k+1} n'^k} S \right\}^2 \cdot \frac{a^2}{(2k-1)^2} 2k(2k-1)(k-1).$$

Hier ist $n_r=0$, $n'_r=0$, $n=3$, $n'=2$, $k=3$, $k'=2$, und

$$\begin{aligned} S &= \int e^{-\frac{5s}{6}} L_{n+k-1}^{2k-1} \left(\frac{2s}{3}\right) L_{n'+k'-1}^{2k'-1} \left(\frac{2s}{3}\right) s^{k+k'-1} ds \\ &= \int e^{-\frac{5s}{6}} L_5^{2} \left(\frac{2s}{3}\right) L_3^{2} \left(\frac{2s}{3}\right) s^6 ds. \end{aligned}$$

Nun gilt

$$L_5^2 \left(\frac{2s}{3}\right) = 5!, \quad L_3^2 \left(\frac{2s}{3}\right) = 3!;$$

daher ist

$$\begin{aligned} S &= \int e^{-\frac{5s}{6}} 5! 3! s^6 \cdot ds \\ &= 5! 3! 6! \left(\frac{6}{5}\right)^7. \end{aligned}$$

Durch Einsetzen der Zahlenwerte ergibt sich

$$I_1 = \frac{2^{10}}{3^5} \cdot \left(\frac{6}{5}\right)^{14} \cdot a^2.$$

Zum wirklichen Vergleich wollen wir $(6/5)^{14}$ fortlassen, da es gemeinsamer Faktor aller Ausdrücke ist.

Für I_2 , Übergang von -2 nach 2 haben wir

$$I_2 = \left\{ \left[\frac{|n_r|}{(n+k)^3} \frac{|n'_r|}{(n'+k'-1)^3} \right]^{1/2} \frac{2^{2k+1}}{3 n^{k+2} n'^{k+1}} S \right\} \cdot \frac{2ka^2}{(2k-1)(2k+1)}$$

mit

$$n_r=0, \quad n'_r=0, \quad k=2, \quad k'=2.$$

Daher ist der Ausdruck in der geschweiften Klammer derselbe in beiden Fällen, da S denselben Wert wie in I_1 hat.

Für I_4 , Übergang von $k=-2$ nach $k=-1$, haben wir

$$I_4 = \left\{ \left[\frac{|n_r|}{(n+k)^3} \frac{|n'_r|}{(n'+k-1)^3} \right]^{1/2} \frac{2^{2k+1} S}{n^{k+2} n'^{k+1}} \right\} \cdot \frac{a^2}{(2k-1)^2} 2k(2k-1)(k-1)$$

$k=2$, $n_r=0$, $n'_r=0$, S hat denselben Wert. Der Ausdruck in der geschweiften Klammer hat denselben Wert wie in I_1 und I_2 .

Wir haben also

$$\begin{aligned} I_1 &: I_2 : I_4 \\ &= \left[\frac{2k(k-1)}{2k-1} \right]_{k=3} : \left[\frac{2k}{(2k-1)(2k+1)} \right]_{k=2} : \left[\frac{2k(k-1)}{2k-1} \right]_{k=2} \\ &= \frac{6 \cdot 2}{5} : \frac{4}{3 \cdot 5} : \frac{4 \cdot 1}{3} \\ &= 9 : 1 : 5. \end{aligned}$$

Das Ergebnis steht mit dem Ornstein-Burger-Sommerfeldschen Gesetz für die Intensitätsverteilung auf die ein $2P-3D$ -Multiplett bildenden Linien in völliger Übereinstimmung.

Man kann auch leicht sehen, dass die Komponenten der Linien $2S-3P$ und $2P-3S$ ebenfalls mit der Ornstein-Burger-Sommerfeldschen Regel in bester Übereinstimmung stehen.

Wir wollen jetzt die Verhältnisse der Intensitätseinheiten in den drei Multipletts suchen.

Nach einiger Rechnung ergibt sich

$$\begin{aligned} I_{PD} &: I_{SP} : I_{PS} \\ &= \frac{I_1}{9} : \frac{I_5}{2} : \frac{I_3}{2} \\ &= 1 : 1,04 : 1,024 \end{aligned}$$

Wir können nun die nach diesen Ergebnissen berechneten Intensitäten für die Komponenten von H_α mit den gefundenen in Fig. 2 vergleichen, die eine Darstellung der Hansenschen Beobachtungen bringt.

Man sieht, dass $I_V/I_R=7,08/9$ ist, während die Beobachtung für die violette Komponente eine et was grössere Intensität als für die rote liefert. Das Ergebnis stimmt also mit den Versuchsergebnissen nicht überein, wenn auch die Abweichung nicht gross ist. Sowohl die violette als auch die rote Komponente erweisen sich als et was asymmetrisch, was wahrscheinlich auf das Vorhandensein von (6) mit der Intensität 1,08 in einer Entfernung von 0,047 Å rechts von der violetten Komponente und von (2) mit der Intensität 1 in einem Abstand von 0,047 Å rechts von der roten Komponente zurückzuführen ist. Die

¹³ $|n|$ bedeutet $n!$

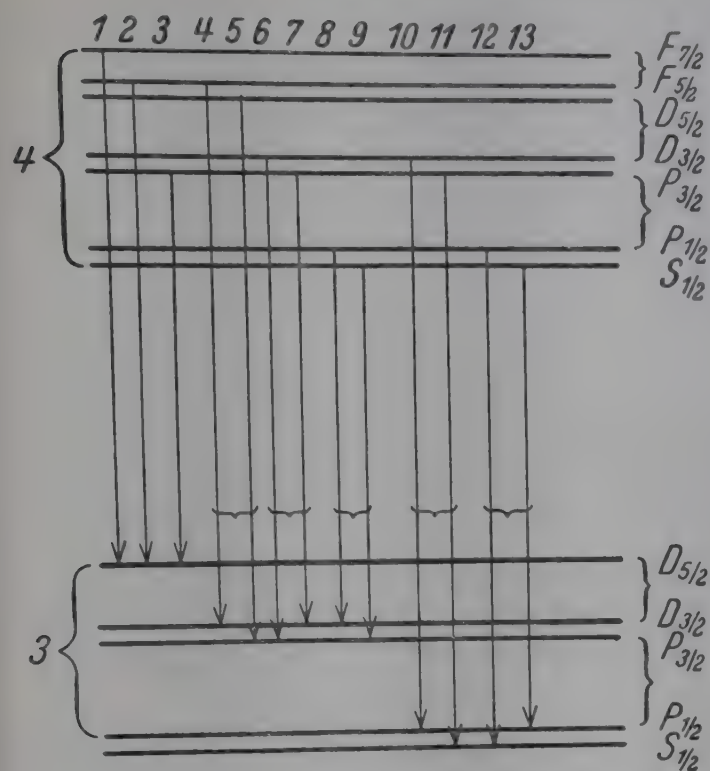


FIG. 4

Komponenten (3) und (7) sind nicht in Betracht gezogen worden, weil sie nur sehr geringe Intensitäten haben.

Die He⁺-Linie $\lambda=4686$. Man kann zeigen, dass die He⁺-Linie $\lambda=4686$ aus den folgenden Multipletts besteht (Fig. 4):

- Das 3 D — 4 F-Multiplett besteht aus (1, 2, 4)
 „ 3 P — 4 D- „ „ (5, 6, 10)
 „ 3 S — 4 P- „ „ (11, 12)
 „ 3 D — 4 P- „ „ (3, 7, 9)
 „ 3 P — 4 S- „ „ (9, 13)

Die Intensitätsverhältnisse in irgendeinem dieser Multipletts nach der Ornstein-Burger-Sommerfeldschen Regel sind durch die mittleren Zahlen angedeutet. So bilden (1, 2, 4) das 3D—4F-Multiplett; die theoretischen Intensitäten sollten sich wie 20:1:14 verhalten; die Goldsteinschen Zahlen sind in diesem Falle nicht wiedergegeben, da sie offensichtlich falsch sind.

Man sieht leicht, dass die Ornstein-Burger-Sommerfeldsche Regel unter den Komponenten eines Multipletts erfüllt ist. Wir wählen das 3D—4F-Multiplett: Wir haben

$$\left[\frac{2k(k-1)}{2k-1} \right]_{k=4} : \left[\frac{2k}{(2k-1)(2k+1)} \right]_{k=4} : \left[\frac{2k(k-1)}{2k-1} \right]_{k=4}$$

$$\frac{8 \cdot 3}{7} : \frac{6}{5 \cdot 7} : \frac{6 \cdot 2}{5}$$

$$20 : 1 : 14$$

in völliger Übereinstimmung mit der genannten Regel. Ähnlich ist sie auch für die übrigen Multipletts gültig.

Verhältnis der Intensitätseinheiten zwischen den einzelnen Multipletts. Eine kleine Rechnung zeigt, dass sich die Verhältnisse der Intensitätseinheiten in den fünf Multipletts folgendermassen ausdrücken lassen:

$$3 D - 4 F : 3 P - 4 D : 3 S - 4 P : 3 D - 4 P : 3 P - 4 S$$

$$1 : 0,85 : 1,11 : 0,025 : 0,225$$

Diese Zahlen stimmen mit den von Sommerfeld und Unsöld gefundenen überein; diese Autoren haben auch gezeigt, dass sie die neuen Paschenschen Beobachtungen an den Feinstrukturkomponenten der He⁺-Linie 4686 vollständig erklären.

Um vergleichen zu können, geben wir die Paschenschen Ergebnisse wieder:

Tabelle 2.

Komponente	Wellenlänge	Intensität ber.	Intensität (Paschen)
3	5,924	0,225 (9·0,025)	? ist vorhanden
verboten	5,890	—	—
1	5,810	20	7
(4,5)	5,710	21,75 (14+9·0,85)	7,5
(12,13)	5,544	1,33 (1,11+0,22)	1
(10,11)	5,384	6,488 (5·0,85+2·1,11)	3

Die Zahlen stammen aus der Paschenschen Arbeit l.c.

Zusammenfassung. Für die Feinstrukturkomponenten von H_a und He⁺-Linie $\lambda 4686$ sind die Übergangswahrscheinlichkeiten unter Verwend der Diracschen Theorie des Elektrons in der Darwin-Weylschen Stellung berechnet worden. Die Ornstein-Burger-Sommerfeldsche Regel für die relativen Intensitäten der ein Multiplett bildenden Komponenten wird aus der Diracschen Theorie abgeleitet. Entgegen den Goldsteinschen Ergebnissen erweist sich die Intensitätsverteilung auf die Feinstrukturkomponenten in guter Übereinstimmung mit Versuchsergebnissen, wie schon Sommerfeld und Ornstein gezeigt haben, indem sie von der Schrödingerschen Form der Wellenmechanik und statistischen Betrachtungen ausgingen.

Zusatz bei der Korrektur. Etwa 1½ Monate, nachdem wir diese Arbeit zum Druck geschickt hatten, erreichte uns eine Arbeit von K. Bechert¹⁴ Über „Die Intensitäten von Dublettlinien nach der Diracschen Theorie“. Bechert behandelt dieselbe Frage und kommt zu genau den gleichen Ergebnissen. Wir müssen nur hinzufügen, dass wir die Intensitäten der Röntgenlinien berechnet haben, wie es

¹⁴ Ann. d. Phys. 6, 700; ausgegeben am 25. September 1930.

auch Bechert im zweiten Teil seiner Arbeit versucht. Der erste Versuch in dieser Richtung stammt von Wentzel¹⁵ in Anlehnung an die Schrödingersche Theorie, und durch diese Arbeit sind Sommerfeld und Unsöld auf die Berechnung der Intensitäten der $H\alpha$ -Komponenten gekommen. Wentzel fand beträchtliche Abweichungen der berechneten Intensitäten von den Versuchsergebnissen von Jönsson und Allison. Man nahm an, dass die Anwendung der Diracschen Theorie diese Unterschiede beseitigen würde. Bei den in dieser Arbeit ausgeführten Berechnungen von (r) vernachlässigten wir $|W| = \alpha Z \cdot |V|$, weil $\alpha = 1/137$ sehr klein ist. Für Röntgenstrahlen liegt aber αZ für die Elemente von Ag bis U zwischen $1/3$ und $2/3$, weswegen W nicht zu vernachlässigen ist. Wir haben für Ag und U Berechnungen angestellt; die berechneten Intensitäten stimmen aber im allgemeinen mit den experimentell beobachteten Werten nicht überein. Der Umstand, dass die Röntgen- und Alkalispektren gleich gebaut sind, hat oft zu der falschen Auffassung geführt, dass sie auf gleiche Art entstehen. Sowohl Wentzel wie Saha und Ray¹⁶ haben auf das

Irreführende dieser Analogie hingewiesen, da ja die Röntgen-niveaus durch das *Fehlen* eines Elektrons in den abgescheuerten Schalen entstehen, während die optischen Niveaus der Alkalimetalle von einem einzelnen ausserhalb der abgeschlossenen Schalen schwingenden Elektron herrühren. Zweitens hängen die Intensitäten der verschiedenen Röntgenlinien, abgesehen von den Übergangswahrscheinlichkeiten, auch von der Wahrscheinlichkeit der Entfernung eines Elektrons aus der $L_1(2s)$ - oder $L_2(2p)$ -Schale durch das äussere Elektronen-bombardement ab. Aber selbst, wenn sich diese beiden Faktoren berücksichtigen liessen, müssten noch weitere Anomalien, wie die Abweichung der Intensitätsverhältnisse der Komponenten irgendeines Multipletts von der Ornstein-Burger-Sommerfeld-Regel erklärt werden (so sollte sich z. B. $\beta_3 : \beta_4$ wie 2:1 verhalten, während es bei U gleich 1:1 ist). Diese Anomalien sind ähnlich den für die Komponenten der höheren Hauptserienglieder bei den Alkalimetallen beobachteten¹⁷ und haben wahrscheinlich dieselben Ursachen (Taubbahnen).

¹⁵ *Naturwiss.* **14**, 1926.

¹⁶ *Phys. Zeit.* **28**, 221, 1927.

¹⁷ Vgl. Sambursky. *Zeit. f. Phys.* **49**, 731, 1928, und E. Fermi, *ebenda*, **59**, 680, 1930.

50. THE SPIN OF THE PHOTON

M. N. SAHA AND Y. BHARGAVA

(*Nature*, **128**, 817, 1931)

Recently a number of papers have appeared on the question as to whether the phenomena of polarisation of light can be explained by the assumption of a 'spin' of the photon.¹ Kastler and Frisch deduce from their experiments that the photon possesses no spin, and Kastler argues further that the phenomena of polarisation should be explained on statistical grounds. Raman and Bhagavantam, on the other hand, argue that the interesting results obtained by Bär and Hanle² on the reversal of the state of polarisation of Raman lines when observed in the direction of propagation of the primary beam can be explained only on the assumption that the photons possess spin. They seem to link circular polarisation definitely with a spin of the photon about the line of propagation.

The arguments of Frisch and Kastler are based upon the Sommerfeld-Rubinowicz explanation of the selection principle for the azimuthal quantum number (principle of conservation of angular momentum of atom plus photon), but applying the same principle, and the principle that the atom-magnet can orient itself in any direction making

certain definite quantised angles with the external field (as proved by Stern and Gerlach's experiment), it can be shown that the absorption of Zeeman components can never disappear with reversal of the field, but it will be modified on passing through two fields, whether parallel or antiparallel. Hence the experiments of Frisch or Kastler cannot be interpreted in the way supposed by them and show no light on the question of the spin. Secondly, and this is more important, a discussion of the Zeeman effect of the π -components of the D_1 line, assuming that the principle of conservation of angular momentum holds during radiation, shows that there may be photons without any 'spin' whatsoever, although they may show polarisation. It therefore seems unjustifiable to describe polarisation with the aid of a 'spin'. It appears that Bär and Hanle's results should be explained in some other way than that proposed by Raman and Bhagavantam.

A full discussion will appear later.

¹ Frisch, *Zeit. für Physik*, vol. 61, p. 626; Kastler, *Jour. de Physique*, May 1931; Raman and Bhagavantam, *Nature*, **128**, July 18, 1931.

² *Naturwiss.*, vol. 19, p. 463, 375; 1931.

Physical Laboratory,
Allahabad, India,

Oct. 14

51. ON THE COLOURS OF INORGANIC SALTS

M. N. SAHA AND S. C. DEB

(*Bull. Acad. Sci., U.P.*, **1**, 1, 1931)

There have been many diverse opinions regarding the origin of colours shown by inorganic salts in the solid state, and in solution. A short summary is given in the 'Handbuch der Physik', Vol. XXIV, p. 564. According to Hoffmann and his co-workers colour is shown only by compounds of such elements which show a varying valency such as Fe, Co, Ni...Ladenberg made the first attempt to connect colour with atom-structure. He showed from analysis of existing data that colour is almost invariably shown by salts of elements belonging to transitional groups (Sc to Cu) and rare-earths, and very seldom by salts of elements belonging to regular groups. Compounds like NaCl, MgCl₂, AlCl₃, SiCl₄,... show no colour, while chlorides of all the elements of the transitional groups (Sc to Cu) show colour. Ladenberg tried to define the electron transition responsible for colour in the following way. He pointed out that in elements from Sc to Cu, the 3d-shell is being formed and there are some electrons in the 4s-shell. He points out that there is some sort of competition between the 3d- and 4s-shells for the possession of electrons, and hence light of very small energy (visible) may be able to effect transition of the electron from any one of these two levels to the other, i.e., from 3d→4s.

Meisenheimer showed that the nature of the anion also has some influence on the colour. Fajans attempted to connect colour with deformation of the cation, produced partly by the anion. He points out that CuF₂ and CuSO₄ (anhydrous) are colourless, and hence concludes that the Cu⁺⁺-ion must be colourless, but in aqueous solution as well as in ammoniacal solutions Cu⁺⁺-ion gives a blue colour. This is ascribed to some deforming action of H₂O or NH₃ molecules on the Cu⁺⁺-ion.

The question of colour forms part of the larger question of binding of atoms of different types to form aggregates of different orders, e.g.—molecules, crystals, solutions; and light is thrown on the problem from many directions, viz., from consideration of the course of refractive index for solids, magnetic properties, or spectral absorption for solids and gases, etc., etc..., and investigation of the same properties in the case of solutions. Pauli's principle has given us the rule governing the formation of atoms out of nuclei and electrons, but the exact way in which it will have to be modified in formation of molecules and

more complex aggregates is not yet known to the satisfaction of the theoretical physicist.

In a note published in 'Nature,' Vol. 125, page 163, one of the authors tried to show that the colours of the salts of the transitional groups may be ascribed to the electrons of the d-shell, but not in the way imagined by Ladenberg. If we take a compound like CrCl₃, we may suppose that the

picture of the combination is given by $\left[\text{Cr}^{+++} \right] \begin{matrix} \text{Cl}^- \\ \text{Cl}^- \\ \text{Cl}^- \end{matrix}$. Thus

there are three chlorine ions surrounding the Cr⁺⁺⁺ nucleus. That this assumption corresponds to the actual picture is almost guaranteed by magnetic properties of CrCl₃. The paramagnetic susceptibility of trivalent chromium compounds is almost entirely due to the Cr⁺⁺⁺-ion, the Cl⁻ ion contributing nothing to the magnetic moment. Hence the colour must be due to the reaction of light either on the electrons or on Cl⁻ ions. But we know that the absorption of the Cl⁻ ion in the vapour state is in the ultraviolet below λ3000, and hence visible light will be without action on the Cl⁻ ions. Hence colour arises from the reaction of light on Cr⁺⁺⁺-ions. This contains, in the free atomic state, an incomplete d³-shell, giving rise to ⁴F, ⁴P, ²H, ²G, etc., terms. What will be the nature of these levels in a compound?

Light is thrown on this question from consideration of the magnetic moment of the Cr⁺⁺⁺-ion. If, following Hund¹, we suppose that the electrons of the d³-shell are bound with the usual 'l' and 's' coupling which gives us the fundamental terms of the Cr⁺⁺⁺-atom, the magnetic moment cannot be explained. Prof. D. M. Bose² showed empirically that the magnetic moment is explained if we suppose that only the 's'-coupling is operative and the 'l'-coupling breaks down in compound formation. Stoner³ has given theoretical justification for this assumption, and explained many other anomalous cases. The breaking of 'l'-coupling can be inferred also from our present knowledge of molecular spectra, where we find that the 'l' vectors of outer electrons get subdivided along the line of binding of the component nuclei while the 's' vectors take up either the parallel or the anti-parallel directions. We can therefore suppose that the action of light consists in changing the spin of one of the component electrons in the d³-shell. The

energy required for this process may be inferred. In the gaseous state, Cr^{+++} -ion gives rise to the following terms:—

$$^4(P\ F),\ ^2(P\ D\ F\ G\ H),\ ^2(D)$$

Cr^{+++} -atom is partially analysed by White and some of the term values are known. They are given in Table I.

The difference in value is of the order for the absorption of visible light not only in Cr^{+++} , but as can be seen from the table (Table II), in almost all ions of the elements of the transitional group.

Table I—Terms of d^3 elements

Term Elements	4F	4P	$^2H_{5,6}$	$^2G_{4,5}$	$^2D_{3,4}$	Reference
Sc						
Ti ⁺	0	8965	11769 11867	8190 8210	11721 11851	H. N. Russell, Astro. Journ., 66, 288 (1927)
V ⁺⁺	0	11513	16822	11966	16229	H. E. White, Phy. Rev., 33, 674 (1929)
Cr ⁺⁺⁺	0	..	21027 21278	15014 15371	..	H. E. White, Phy. Rev., 33, 676 (1929)
Mn ⁺⁺	0	..	24395 25361	17852 18468	..	H. E. White, Phy. Rev. 33, 679 (1929)

Table II—Difference between the highest and the next term with lesser-multiplicity

Stage of Ionisation Elements	II	III	IV	V
Sc				
Ti	11800	14500		
V		16800	19087	
Cr			21000	23237
Mn				25000

[II, III, IV, V denote first, second, third and fourth state of ionisation.]

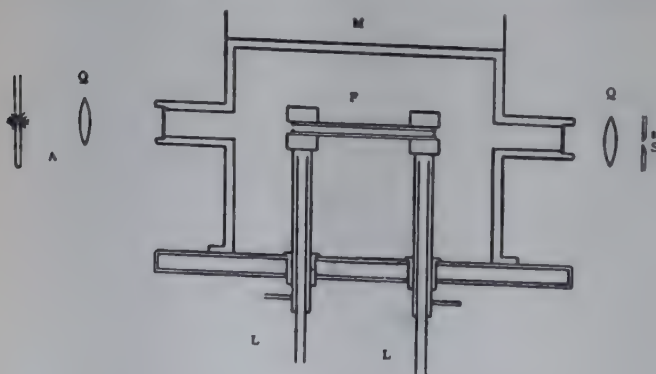


Fig. 1. F—Furnace, M—Iron mantle, Q—Quartz lens, A—Under water copper spark, L—Leads for heavy current, S—Slit for spectrograph.

A number of experiments can be designed to test this hypothesis. Owing to the limitations of this laboratory we undertook investigation of the absorption spectrum of a few chlorides of the transitional group.

Experimental Procedure

We chose as our first experimental material CrCl_3 . This is obtained in pink-coloured scales, and according to information obtained from standard treatises on Chemistry, it forms a stable vapour at $1200^\circ\text{--}1350^\circ\text{C}$, whose vapour density corresponds to the formula CrCl_3 . It does not decompose up to a temperature of 1500°C .

F is a vacuum furnace of acheson graphite used in this laboratory for experiments on the thermal ionisation of elements. The CrCl_3 was placed within a silica tube which was placed within the furnace. This was to prevent direct contact of the carbon of the furnace with CrCl_3 . The ends of the furnace were plugged with iron rings leaving only narrow opening in the centre for passage of light. These rings prevented quick outflow of hot vapour. The evaporation of CrCl_3 is so rapid that the whole mass disappears before any exposure can be given. When the furnace is filled with N_2 the conditions could be kept steady.

Source of continuous light was an under water-spark between two copper electrodes. The rays from the spark were made parallel with a quartz lens and allowed to pass through the furnace over the hot vapour of CrCl_3 and on emergence again focussed on the slit of an E_1 quartz spectrograph, kindly lent to us by Prof. N. R. Dhar of the Chemistry Department. Copper arc was taken as comparison spectrum. The spectrum was examined between $\lambda 5000$ to $\lambda 2400\text{ \AA}$.

Absorption bands were obtained in the blue-violet region extending slightly into the ultraviolet. They were analysed and are seen to form two distinct systems which we depict below by A and B systems. Following is the analysis of the bands:

Table III—System A

ν' \ ν''	0	1	2	3	4
0	22654.5	22241.7	21828		
1	23067	23652	22236	21824	
2	23477	23062	22646	22232	21822
3	23883	23472	23059		
4		23874	23468	23054	
5			23869	23462	

This system of bands can be represented in the following formula:

$$\nu_{\text{head}} = 22654.5 + (414.07\nu' - 87\nu'^2) + (414.2\nu'' - 60\nu''^2)$$

The second system of bands which we designate by "System B" is given below:

Table IV—System B

$\nu' \backslash \nu''$	0	1	2	3
0	22545.1	22117	21689	
1	22958	22525	22093	
2	23352	22926		
3	23741	23318	22907	
4		23699		

The above set of bands is also represented in an empirical formula which we give below:

$$\nu_{\text{head}} = 22545.1 + (414.0\nu' - 4.7\nu'^2) + (431.2\nu'' - 3.65\nu''^2)$$

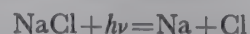
In addition to these band absorptions, continuous absorption was obtained near $\lambda 3000 \text{ \AA. U.}$, and the spectrum is completely cut off at $\lambda 2700 \text{ \AA. U.}$

Table V—List of absorbed band heads

λ	ν (vac)	System	Classification $\nu'' - \nu'$
4185.8	23883	A	0—3
4187.4	23874	A	1—4
4188.3	23869	A	2—5
4210.7	23742	B	0—3
4219.4	23699	B	1—4
4258.25	23477.2	A	0—2
4259.2	23472	A	1—3
4260.0	23468	A	2—4
4260.9	23462	A	3—5
4280.8	23352	B	0—2
4287.3	23318	B	1—3
4333.88	23067.5	A	0—1
4334.9	23062	A	1—2
4335.5	23059	A	2—3
4336.4	23054	A	3—4
4354.3	22958	B	0—1
4360.6	22926	B	1—2
4364.2	22907	B	2—3
4412.90	22654.5	A	0—0
4413.39	22652.1	A	1—1
4414.5	22646	A	2—2
4434.34	22545.1	B	0—0
4438.2	22525	B	1—1
4494.80	22241.7	A	1—0
4495.9	22236	A	2—1
4496.8	22232	A	3—2
4520.0	22117	B	1—0
4525.0	22093	B	2—0
4580.1	21828	A	3—1
4580.9	21824	A	4—2
4581.3	21822	A	2—0
4609.3	21689	B	

Discussion of the Results

A large amount of work has been published on the absorption spectra of the halides. Two types of absorption have been found. In the case of saturated halides of alkali elements only a continuous absorption is obtained. Franck, Kuhn and Rollefson⁴ have shown that the beginning of absorption corresponds to the photodissociation of the halide-molecule into constituent atoms:



ν corresponds to the atomic heat of dissociation:—



R is calculated from a Born-cycle. We have

$$R = Q + L_{\text{Na}} + \frac{1}{2}D_{\text{Cl}_2} - L_{\text{NaCl}} \quad \dots \quad (1)$$

where Q = heat of formation of solid NaCl out of solid Na and Cl_2 gas, L_{Na} is the latent heat of evaporation of Na, D_{Cl_2} is the heat of dissociation of Cl_2 , and L_{NaCl} is the heat of evaporation of NaCl.

Franck has shown that most alkaline halides give the same kind of results as NaCl; he assumes that in these compounds, the valency electron of Na passes over to Cl, thus the binding is electrostatic; due to attraction between Na^+ and Cl^- or polar. When light falls on an NaCl-molecule, the electron in Cl^- passes on to N^+ —thus resulting in dissociation of NaCl to neutral Na and neutral Cl.

But there are other chlorides like HCl⁵ which show a continuous absorption, but the beginning of absorption does not correspond to the heat of formation of HCl out of H and Cl.

A second class of chlorides like AgCl,⁶ ThCl,⁷ etc., shows band absorption in addition to the continuous absorption. The band absorption in such cases has not been satisfactorily explained.

Very little work has so far been done on the band-spectra of polyatomic halides, but a few experiments have been carried out in this laboratory (*vide* papers by A. K. Dutt and M. N. Saha, S. C. Deb and H. B. Mohanti). It appears from these works that all saturated halides like MgCl_2 , AlCl_3 , . . . show only continuous absorption, and if ν denotes the frequency of the beginning of absorption

$$h\nu = \frac{R}{n}, \quad \dots \quad (2)$$

where R = heat of formation of the gaseous molecule out of constituent atoms, n = valency.

$$R = Q + L_{\text{M}} + \frac{n}{2}D_{\text{Cl}_2} - L_{\text{MCl}_n} \quad \dots \quad (3)$$

On the other hand, it appears that non-saturated halides like CrCl_3 , as well as halides of Ca, Sr, Ba (*vide* forthcoming paper by S. C. Deb and B. Mukerji) give, in addition to continuous absorption, well marked band absorption. The continuous absorption seems to be due to the splitting up of a Cl-atom from the molecule. We may try to find out

when (3) holds in the case of CrCl_3 in absorption. We have

$$R = Q + L_{\text{Cr}} + \frac{3}{2}D_{\text{Cl}_3} - L_{\text{CrCl}_3} \quad \dots \quad (4)$$

Q , the heat of formation of $[\text{CrCl}_3]$ out of $[\text{Cr}]$ and Cl_2 , is about 145 kcal, but neither L_{Cr} nor L_{CrCl_3} is known. Hence (4) cannot be tested.

Band Absorption

The band absorption of CrCl_3 is certainly due to the reaction of light on the d^3 -shell of the Cr^{+++} -ion. As is known from theories of complex spectra, the spin moments of all the electrons in the normal state for the d^4 -shell are parallel giving rise to a 2X -term ($X=F, P, \dots$ when Pauli's principle is operative). The action of light would be to turn the spin of one of the electrons in the opposite direction giving us a 2Y -term. Thus the magnetic moment of the Cr^{+++} -ion on light absorption will be changed from $\sqrt{4S(S+1)} = \sqrt{4 \cdot \frac{3}{2}(\frac{3}{2}+1)}$, i.e., from $\sqrt{15}$ to $\sqrt{3}$, i.e., will get changed by about 2.5 times per quantum absorbed. The effect has been qualitatively found by Prof. D. M. Bose⁸, but contrary to expectation, the magnetic moment of CrCl_3 solutions is found to increase on illuminations by light which can be absorbed. Prof. D. M. Bose is of opinion that the increase is

due to the supposed fact that the coupling of the d -electrons of the paramagnetic ions with the associated water molecules, known as l -coupling is broken down by the act of light absorption.

The suggestion is rather vague. An alternative suggestion may be made. It is known from the works of Herzberg that in molecule formation, atoms are not always in their lowest state. Thus in SiN as well as in CN , the silicon and carbon atoms are in the 4D_2 -state, and not in the 3P -states which are deeper. Probably in CrCl_3 the d^4 -shell of Cr^{+++} -ion is in the 2Y -state, i.e., the spins of two electrons oppose each other. When light falls, the molecule breaks up, and the Cr^{+++} -ion takes up the more stable condition in which the electrons have their spins in the same direction.

REFERENCES

- ¹ Hund, *Linien spektren and periodische System* (Springer, Berlin, 1927.)
- ² D. M. Bose, *Zeits. f. Physik*, **63**, 864, 1927.
- ³ Stoner, *Phil. Mag.*, **8**, 250, 1929.
- ⁴ Franck, Kuhn and Rollefson, *Zeits. f. Physik*, **48**, 155, 1927 et seq.
- ⁵ Cohen and Stuckardt, *Zeits. f. Phys. Chem.*, **91**, 722, 1927, and Tingey and Gerke, *Am. Chem. Soc. J.*, **43**, 1838, 1926.
- ⁶ Franck and Kuhn, *Zeits. f. Physik*, **43**, 155, 1927 and **44**, 606, 1927; Brice, *Phy. Rev.*, **35**, 960, 1930.
- ⁷ Butkow, *Zeits. f. Physik*, **58**, 232, 1930.
- ⁸ D. M. Bose and P. K. Raha, *Nature*, **128**, 520, 1931.

52. ON THE ABSORPTION SPECTRA OF SATURATED HALIDES OF MULTIVALENT ELEMENTS

A. K. DATTA AND M. N. SAHA

(*Bull. Acad. Sci., U.P.*, **1**, 19, 1931)

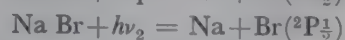
The absorption spectra of alkali halides in the vapour state have received a good deal of attention in recent years from Angerer and Müller,¹ Müller,² Franck, Kuhn and Rollefson.³ They found that the absorption spectra were strictly continuous, i.e., started from a rather ill-defined long wavelength limit and stretched towards the ultraviolet. In the case of bromides and iodides, two absorption maxima were noted. In some cases there was re-transmission of the spectrum in the shorter wavelength side. Franck showed that the long wavelength limit of the continuous spectrum marks the photo-dissociation of the molecule into neutral atoms according to the scheme



$$Nh\nu = D$$

D =heat of dissociation calculated from a Born-cycle.

In the case of bromides and iodides the molecule, in addition may decompose into an excited halogen atom and a metallic atom, according to the scheme



This gives rise to a second absorption-beginning, removed to the short wavelength side by the difference $\Delta\nu = ^2P_{3/2}^o - ^2P_{1/2}^o$. This is present also in the case of chlorine, but as $\Delta\nu$ is small in this case, it cannot be distinguished from the first absorption-beginning. But in the case of NaBr and NaI , they obtain two absorption maxima, separated by the distance $\Delta\nu = ^2P_{3/2}^o - ^2P_{1/2}^o$, from which they conclude that the molecule NaBr decomposes into Na and $\text{Br}(^2P_{3/2}^o)$ and Na and $\text{Br}(^2P_{1/2}^o)$. (*Vide* Fig. 34, p. 230, Photo Processes by Griffiths and Mckeown).

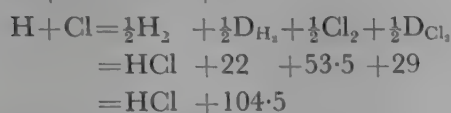
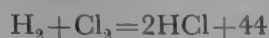
The same consideration would hold also for hydrogen

halides⁴, but here the agreement is not good, as can be seen from the following table:—

TABLE 1

Substances	Q (Heat of Formation)	R _{calc} (Atomic Heat of Formation)	λ Observed long wave- length limit of absorption	R _{obs}
HCl	22.0	105	2350	122
HBr	8.6	84	2640	108
HI	2.89	76	3320	86

The calculation of R in the third column is as follows:—



Hence R = 105 kcal.



The discrepancy between R calculated from photo-dissociation according to Franck's idea and R experimentally obtained is too large and is beyond experimental error. Hence Franck's rule does not seem to apply to the hydrogen halides. Franck is of opinion that the binding in HCl is non-ionic. A difficulty appears in the interpretation of the dipole moment of HCl molecule. The distance between the nuclei is found to be 1.28×10^{-8} cm. from an analysis of the rotation spectrum of HCl, but the dipole moment is found to be 2×10^{-18} units. If we suppose that HCl consists of H^+ and Cl^- ions forming a closed shell, then μ , the dipole-moment, ought to be 3 times larger, being $1.28 \times 10^{-8} \times 4.70 \times 10^{-10} = 6 \times 10^{-18}$. Hence the presumption is that in HCl, the electron does not completely leave H and attach to Cl, giving rise to an ionic compound. But it is not completely atomic as in that case μ should be nil.

Another class of halides, like AgCl^3 and ThCl_4 ,⁴ give band absorption in addition to continuous absorption. These facts have not yet been satisfactorily explained.

No systematic investigation of the absorption spectra of the poly-atomic saturated halides has been undertaken so far, excepting some previous work of Evans⁷ and Leifson⁴. The present work was taken up to see the implications of the above ideas in the case of the poly-atomic compounds. The halides so far investigated by us are CCl_4 , SiCl_4 , SnCl_4 , TiCl_4 . These were chosen because they are usually volatile liquids and a large vapour pressure can be easily obtained.

For carrying out the experiment, an absorption tube of ordinary glass was used; to this was attached a bulb which

contained the liquid under investigation. At first the quartz plates were fitted with sealing wax, but as it was attacked by chlorides, soluble silicate of soda was used to fix up the plates. For this the ends of the tube must be well ground. The spectrographs used were a Hilger E_3 and a bigger Zeiss apparatus corresponding to E_2 of Hilger but with greater light gathering power. The source of continuous light was underwater spark of copper. Good continuous spectrum reaching up to λ 2000 was obtained after an exposure of 3 minutes in the E_3 and 5 to 7 minutes in the Zeiss apparatus.

All the spectra showed continuous absorption and no trace of bands. In the case of SnCl_4 re-transmission was obtained for a short region after the first absorption beginning. The nature of re-transmission varies with vapour pressure and the points need further careful investigation. The preliminary results are shown in the following table:—

TABLE 2

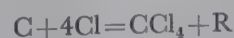
Results of experiment with tetra-halides

Substance	λ Long- wave limit	Q _m in kcal	L _m of the ele- ment	2.DCl ₂	Q heat of forma- tion	R	R/4
CCl_4	240 μμ	118	282	58×2	68.5	466.5	117
SiCl_4	280 „	102	—	„	121.8	..	..
TiCl_4	328 „	87	—	„	—	..	..
SnCl_4	386 „	74	73.9	„	118	308	77

The second column gives the experimentally obtained values of λ and the third column gives the corresponding values of Q_m obtained from the quantum relation

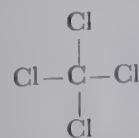
$$Q_m = Nh\nu_m/J$$

In column 7, we have given the value of R, the atomic heat of formation of the molecule. R may be defined by the reaction



where all the substances are supposed to be in the gaseous state and C and Cl are atomic. It is seen from comparison of columns 3 and 7 of the Table 2 that R is nearly $4Q_m$ in the cases where the data are available, and this is the main result obtained from the present investigation. The explanation seems to be quite simple.

In a CCl_4 molecule, the structure may be imagined to be given by



If in continuation of Franck's argument we assume that

TABLE 3

Element	L_m Heat of Sublimation	$\frac{n}{2} = D_{Cl_2}$	Q Heat of Formation	L_{com} Heat of Sublimation of the chloride	R	$\lambda = \frac{R}{n}$
Be	..	57	112	..	..	..
Mg	47	..	151	..	255 — L_{com}	..
Ca	44.2	..	190.3	..	291.5 — L_{com}	..
Sr	..	..	195.6	..	..	..
Ba	..	..	197	..	..	..
Zn	31.3	..	97.2	..	185.5 — L_{com}	..
Cd	27	..	93.2	10.5?	..	..
Hg	15.5	..	53.5	16.9?	..	..
B	..	84	(90)	..	..	..
Al	48	84	161	28?	..	..
In	..	..	128	..	..	..
Tl	38.2	..	80	..	202.2 — L_{com}	..
Pb	46	114	..	..	..	..

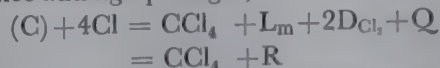
the effect of light, producing continuous absorption in vapour, is to drive out one Cl atom from the molecule, then $h\nu_m = \frac{1}{4}R$ as the total R can be supposed to be equally distributed amongst all the 4 C-Cl bondages. The investigation seems to confirm this view.

R in the seventh column of the Table 2 has been calculated from the following reaction—

$$(C) = [C]_{Dia} + L_m$$



Hence adding up we get,

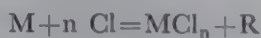


L_m in the case of carbon has been taken from a calculation by Fajans from the vapour pressure of carbon as determined by Lummer. For the heat of dissociation of Cl_2 the latest accepted value by Franck has been taken. The value of Q has been taken from Landolt and Börnstein's tables [p. 1500, (1923)]. They are due to Thomsen.

For $SiCl_4$, the value of L_m is still lacking. If the present ideas hold the value of L_m comes up as 178.2 kcal—a fairly probable value.

For $SnCl_4$ the value of L_m is 73.9 kcal and is due to Greenwood and $Q = 118$ kcal (L and B tables).

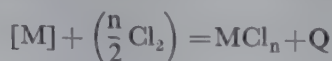
It cannot be said, however, on account of the uncertainty in some of the data* used, that the relation $R = 4Q$ has been established. If it is true, we should expect that generally $R = nQ$ where we are treating a saturated poly-atomic halide with n chlorine atoms. R is the heat of reaction in the process.



and is equal to $L_m + \frac{n}{2} D + Q - L_{com}$, where L_m is the heat of evaporation from the solid state to the monatomic gas state.

D = heat of dissociation of Cl_2

Q = heat of reaction in the process



We can test the possibilities in some of the poly-atomic halides. The available data are given in the following table.

In the case of di-valent halides the latent heat of the compound is not known excepting in the case of $HgCl_2$ for which it has been calculated from vapour pressure data. The absorption spectrum of $HgCl_2$ was studied by Evans and has again been studied recently in this laboratory by Deb and Mohanty. Without entering into details, it may be said that the results of the experiments do not agree with our theory. We should get continuous absorption at $\lambda = 5280$, while Evans finds the beginning at $\lambda = 3500$ while

Deb and Mohanty find that the absorption begins at $\lambda = 2500$. The data are therefore contradictory. But no trace of absorption has been found at the expected point. Fresh light has been thrown on the question of binding from the study of Raman effect of the chlorides. It has been found that the chlorides can be divided into two groups. Firstly, those which do not show Raman scattering and to this group belong most of the ionic compounds, NaCl for example.* Secondly, those which show Raman scattering. To this group belong most of the atom compounds including $HgCl_2$. But it must be remembered that Raman effect has been studied only in the solid state and hence it may not be safe to deduce any conclusion from it regarding the nature of binding. Anyway, there may be expected some discrepancies in the case of some molecules, just as HCl does not fall in line with NaCl and other compounds. The subject is receiving further consideration.

REFERENCES

- * Raman effect for NaCl has however been recently obtained by Fermi and Rasetti, *Zeits. f. Physik*, **71**, 689, 1931.
- ¹ Angerer and Müller, *Phys. Zeit.*, **26**, 643, 1925.
- ² Müller, *Ann. der Phys.*, **82**, 39, 1926.
- ³ Franck, Kuhn and Rollefson, *Zeits. f. Physik*, **43**, 155, 1927.
- ⁴ Leifson, *Astro. J.*, **63**, 73, 1926 and Tinge and Gerke, *Am. Chem. Soc. J.*, **48**, 1838, 1926.
- ⁵ Franck and Kuhn, *Zeits. f. Physik*, **43**, 164, 1927; Brice, *Phys. Rev.*, **35**, 960, 1930.
- ⁶ Butkow, *Zeits. f. Physik*, **58**, 232, 1930.
- ⁷ Evans, *Phil. Mag.*, **31**, 55, 1915.

* The uncertainty mostly refers to the latent heat of the element. Thus L_m for C is given for all values from 146 kcal to 280 kcal.

53. ON THE INTERPRETATION OF X-RAY TERM VALUES

M. N. SAHA AND R. S. SHARMA

(*Bull. Acad. Sci., U.P.*, **1**, 119, 1931)

Received January 24, 1931.

INTRODUCTION

1. The object of the present paper is to offer a rather radically different interpretation of the X-ray term-values than what is at present usually accepted. The present view-point has been summarized by Pauling and Goudsmit in their book on "Structure of Line Spectra, Chap. X." It is well-known that the diagrammatic lines of X-ray spectra show the same structure as alkali-spectra, and this has given rise to the widespread belief that the X-ray term-values and their differences can be calculated¹ in the same way as term-values for hydrogen or the alkalis, after the introduction of suitable screening constants. But it was pointed out by M. N. Saha and B. B. Ray² that the apparent analogy of X-ray spectra to alkali spectra is rather misleading. It is due to the operation of the Pauli Exclusion Principle which says that defect of a single electron from a closed shell gives rise to the same spectroscopic levels as the presence of one single electron outside a closed shell. Thus $2p^5 \dots 5$ electrons in the L-shell give rise to the spectroscopic level $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$, while one p electron also gives rise to the same levels. Since the X-ray spectra are due to the removal of an electron from some level, and the subsequent jumping of an electron from some outer level to this, it follows that the term-values have to be calculated in a widely different way than that usually followed.

CALCULATION OF TERM-VALUES

2. To illustrate the above point of view, let us take the procedure usually adopted for calculating ν_K , ν_{L_1} , $\nu_{L_{21}}$, $\nu_{L_{22}}$ etc. Now $h\nu_K$ represents the energy required to remove one electron from the K-shell to infinity, hence the theoretical problem before us is to find out the total energy of an electron in the K-shell. This electron moves in the field of force composed of that due to the central charge $+Ze$, the field due to the companion-electron in the K-shell and the field due to the outer electrons. If the field due to the outer electrons could be neglected, we shall have just the helium problem with the central charge equal to $+Ze$. We specially insist that the field due to the companion in the K-shell be treated separately, as this being in the same quantum orbit, produces much greater effect than other

electrons. Hence ν_K should correspond to the 1S_0 term of He. In no case, can it correspond to the $^2S_{\frac{1}{2}}$ term of hydrogen, as is usually accepted. But the field due to the outer electrons cannot be neglected, hence the actual problem becomes more complicated than that of helium.

These considerations apply equally well to the calculation of the term-values for L_{11} , L_{21} , L_{22} ; for L_{11} we find that it corresponds to the 1S_0 term of Be, the central charge being different. The $\nu_{L_{21}}$ term corresponds to the removal of an electron from the $2p^6$ shell giving rise to the 1S_0 state. For $Z=10$, when the $2p^6$ shell is completed, this corresponds to the 1S_0 -term of Neon. Hence L_{21} -values have to be linked to the 1S_0 -term of Neon.

The difference $\nu_{L_{21}} - \nu_{L_{22}} \dots$ is usually referred to the $\Delta\nu$ -difference for the 2P terms of hydrogen, but according to the present stand-point, this is to be explained on the same basis as to the $(^2P_{\frac{3}{2}} - ^2P_{\frac{1}{2}})$ differences of F, Ne^+ , $Mg^{++} \dots$

These ideas involve a complete re-calculation of the term-values in X-ray spectra on a basis very different from that followed at the present time.

Before embarking on this venture, we want to present a complete survey of the experimental material.

3. *The screening constant for the K-level.*—Usually ν_K , the value of the absorption limit is represented by the formula

$$\sqrt{\frac{\nu_K}{R}} = \frac{Z - \sigma_K}{1}, \quad (1)$$

where σ_K is known as the screening constant for the K-level.

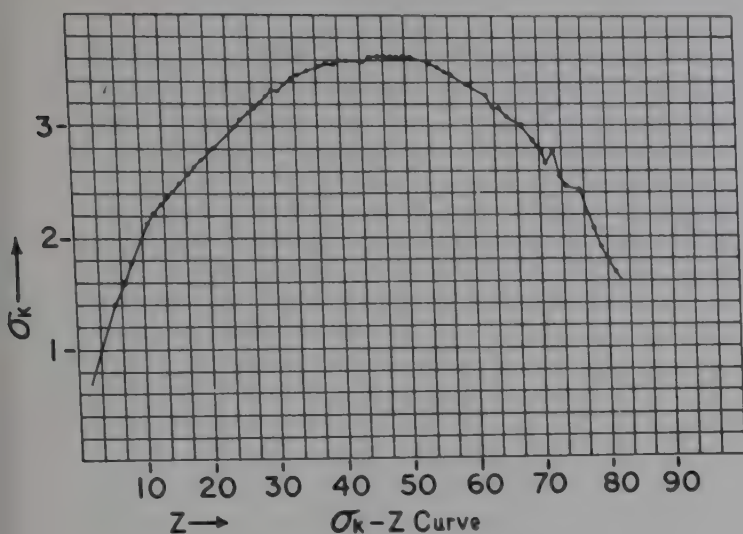
It was at first thought³ that σ_K was nearly constant, viz., 3.4, for all elements, but this impression was due to the fact that data regarding only a few elements were available. In Table 1, we have collected all the available data regarding σ_K and these have been plotted in Fig. 1.

The values of ν_K from 92Ur to 12Mg were taken from Lindh, *Hundbuch d. Exp. Physik*, Vol. XXIV, p. 196, and σ_K was calculated according to (1). The values of σ_K for elements below Mg are subject to a certain amount of uncertainty, as a regular K_α -line can be obtained only when the L_2 -level is complete. In cases where L_2 is not completed, K_α -line shows increasing diffuseness. The

Table 1.—Screening constant for the K-level

Z	σ_K calc.	σ_K obs.	Diff.	Z	σ_K calc.	σ_K obs.	Diff.
2 He*	..	.657	..	48 Cd	3.63	3.642	+0.012
3 Li ⁺	..	.85	..	49 In	3.62	3.644	+0.024
4 Be	..	1.19	..	50 Sn	3.61	3.637	+0.027
5 B	..	1.286	..	51 Sb	3.60	3.629	+0.029
6 C	1.59	1.43	-.16	52 Te	3.58	3.616	+0.036
7 N	1.69	1.60	-.09	53 I	3.56	3.602	+0.042
8 O	1.797	1.77	-.027	54 Xe	3.53	..	..
9 F	1.898	1.894	-.004	55 Cs	3.51	3.535	+0.025
10 Ne	2.089	..	..	56 Ba	3.48	3.508	+0.028
11 Na	2.09	2.13	+0.04	57 La	3.45	3.481	+0.031
12 Mg	2.18	2.21	+0.03	58 Ce	3.42	3.452	+0.032
13 Al	2.270	2.30	+0.03	59 Pr	3.38	3.39	+0.01
14 Si	2.357	2.36	+0.003	60 Nd	3.34	3.413	+0.073
15 P	2.44	2.44	0.0	61	3.30	..	..
16 S	2.52	2.51	-.01	62 Sm	3.25	3.28	+0.03
17 Cl	2.598	2.58	-.018	63 Eu	3.20	3.18	-.02
18 A	2.673	2.65	-.023	64 Gd	3.15	3.17	+0.02
19 K	2.755	2.70	-.055	65 Tb	3.097	3.08	-.017
20 Ca	2.815	2.78	-.035	66 Dy	3.05	3.07	+0.02
21 Sc	2.815	2.80	-.015	67 Ho	2.98	3.023	+0.043
22 Ti	2.88	2.87	-.01	68	2.92	..	..
23 V	2.945	2.93	-.015	69 Th	2.85	2.89	+0.04
24 Cr	3.01	3.00	-.01	70 Yb	2.78	2.77	-.01
25 Mn	3.06	3.05	-.01	71 Lu	2.72	2.66	-.06
26 Fe	3.12	3.12	0	72 Hf	2.64	2.77	+0.13
27 Co	3.17	3.15	-.02	73 Ta	2.57	2.55	-.02
28 Ni	3.22	3.23	+0.01	74 W	2.49	2.46	-.03
29 Cu	3.27	3.28	+0.01	75	2.41	..	..
30 Zn	3.31	3.33	+0.02	76 Os	2.32	2.42	+0.1
31 Ga	3.35	3.33	-.02	77 Ir	..	..	..
32 Ge	3.39	3.41	+0.02	78 Pt	2.14	2.08	-.06
33 As	3.43	3.436	+0.006	79 Au	2.04	1.92	-.12
34 Se	3.46	3.471	+0.011	80 Hg	1.95	1.82	-.13
35 Br	3.49	3.495	.005	81 Tl	..	1.67	..
36 Kr	3.52	..	..	82 Pb	..	1.61	..
37 Rb	3.55	3.543	-.007	83 Bi	..	1.50	..
38 Sr	3.57	3.561	-.01	84 Po	..	..	..
39 Y	3.585	3.56	-.025	85	..	..	..
40 Zr	3.60	3.59	-.01	86 Niton	..	..	..
41 Nb	3.62	3.601	-.019	87	..	..	..
42 Mo	3.63	3.615	-.015	88 Ra	..	..	..
43	..	..	..	89 Ac	..	.24	..
44 Ru	3.64	3.6	-.04	90 Th	..	..	..
45 Rh	3.64	3.652	+0.012	91 Utl	..	..	..
46 Pd	3.64	3.644	+0.004	92 Ur	..	-.07	..
47 Ag	3.64	3.645	+0.005				

*Skinner, *Nature*, Feb. 6, 1932.†Lindh, *Handbuch d. Exp. Physik*, XX, p. 373 (Electron bombardment method).

Fig. 1—Showing the relation between σ_K and Z

K-limits have been measured directly by Thibaud⁴ for C, N, O. For the other elements, we have slightly increased the frequency values for the K_α -line which have been observed by a number of investigators.⁵ Helium is the element giving the first K-series, as it has two electrons in the K-shell. Hence ν_K for He corresponds to the ionisation potential of He, *viz.*, 24.5 volts. The curve shows that the σ_K -curve is continuous up to He. This is a proof of the essential correctness of our method of representing the ν_K -limits.

The (σ_K/Z) curve is approximately parabolic, with small kinks at places where a shell becomes complete, and a new shell begins, *e.g.*, at 20 Ca, $\sigma_K=2.78$ while for 21 Sc, $\sigma_K=2.80$.

In Sc, the 3d-shell is beginning to be formed. The value becomes approximately constant for 37Rb to 56Ba [3.54–3.64–3.48] and this gave rise formerly to the belief that σ_K was constant for all elements. But beyond Ba, σ_K rapidly diminishes, and at 92U, σ_K actually becomes negative, *i.e.*, there is no screening at all.

' σ ' can be roughly represented by the formulae

$$\left. \begin{aligned} \sigma_K &= .895 + .124Z - .0014Z^2 \text{ up to } Z=20 \\ \sigma_K &= .895 + .124(Z-1) - .0014(Z-1)^2, Z=20 \text{ to } 92 \end{aligned} \right\}. \quad (2)$$

The differences between observed and calculated values² are shown in Table 1.

4. *Causes of Screening*—According to the ideas developed here, ν_K should be calculated from the equation

$$\nabla_1^2 \psi + \nabla_2^2 \psi + \frac{8\pi^2 m}{h^2} \left[W + \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}} + V \right] \psi = 0, \quad (3)$$

where ∇_1, ∇_2 correspond to the two K-electrons (3), and r_1, r_2 are their respective distances from the nucleus, W = total energy of the two K-electrons, V is the potential due to the outer electrons and r_{12} the distance between the two electrons. If V were zero, the problem would have reduced

to the helium one which has been completely solved by Heisenberg, and numerical formula for the calculation of W has been given by Kellner and Hylleras.⁶ $W = E_1 + E_2$ = sum of the energies of the two electrons. Hylleras gives the following formulae for the ionisation potential of the electrons in the helium shell:

$$\begin{aligned} \frac{E_1}{R\hbar} &= \left[Z^2 - \frac{5}{4}Z + .31488 - .01752 \frac{1}{Z} + \frac{.00548}{Z^2} \right], \\ \frac{E_2}{R\hbar} &= (Z+1)^2. \end{aligned} \quad (4)$$

The formula (4) is in excellent agreement with experimental data due to Edlen.⁷ This is shown in Table 2 below.

TABLE 2

	He	Li	Be
I.P. calculated	24.47	75.272	153.140
I.P. observed	24.467	75.219 $\pm$.012	153.09 $\pm$.10

For finding out the value of ν_K , the value of V must be found. Various methods for determining the value of the potential field in the inside of atoms have lately been developed, and the one due to Fermi⁸ seems to be the most promising. But the mathematical difficulties in the solution have not yet been overcome.

We may, however, compare the values of ν_K as experimentally obtained, with the value of the I.P. of the helium like stripped atoms of the group He to Na. This will give us some idea of the outer screening due to the L-electron shell, as this is being formed by the addition of successive electrons. The comparison is shown in Table 3.

TABLE 3

Element	I.P. of Stripped Atoms	$\frac{\nu}{R}$	σ	$\frac{\nu_K}{R}$	σ_K
2 He	24.45	1.81	.655	1.802	.657
3 Li ⁺	75.272	5.56	.642	3.89	1.03
4 B ⁺⁺	153.09	11.30	.637	7.87	1.195
5 B ⁺⁺	258.0	19.05	.634	13.80	1.285
6 C ⁺⁺	390.0	28.81	.632	20.90	1.428
7 N ⁺⁺	..	..	..	29.3	1.59
8 O ⁺⁺	..	..	..	38.8	1.77
9 F ⁺⁺	..	..	..	50.5	1.894
10 Ne ⁺⁺	..	..	..	..	2.019

The second column contains the value of the I. P. of the stripped atom, the third shows corresponding ν/R of the stripped atom from which σ in the fourth column has been calculated taking $\sqrt{\frac{\nu}{R}} = Z - \sigma$; we find that σ varies gradually from .655 to .625. This is in accordance with Hylleras' formula.

In the fifth column, we have values of ν_K/R and the sixth column shows σ_K . It is seen that $\sigma_K > \sigma$ and increases with the number of L-electrons steadily, but on the lower limit $\sigma_K \rightarrow \sigma$ for He. Thus it is apparent that the outer electrons contribute very essentially to the screening, as was first pointed out by Bohr.

5. The ν_{L_1} -values.—The values of the ν_{L_1} -level are given by Lindh⁸ up to 37 Rb. For other elements, the absorption limit has not yet been obtained, but we can determine ν_{L_1} from the relation

$$\nu_{L_1} = \nu_{\beta_3} + \nu_K - \nu_{K\beta}. \quad \dots \quad (5)$$

In this way ν_{L_1} has been calculated for 26 Fe, 28 Ni, 29 Cu and 33 As, from Thoræus' measurement of $L\beta_3$. The ν_{L_1} and σ_{L_1} values are shown in Table 4, and σ_{L_1} 's are

$\sigma_{L_1} - Z$ Curve

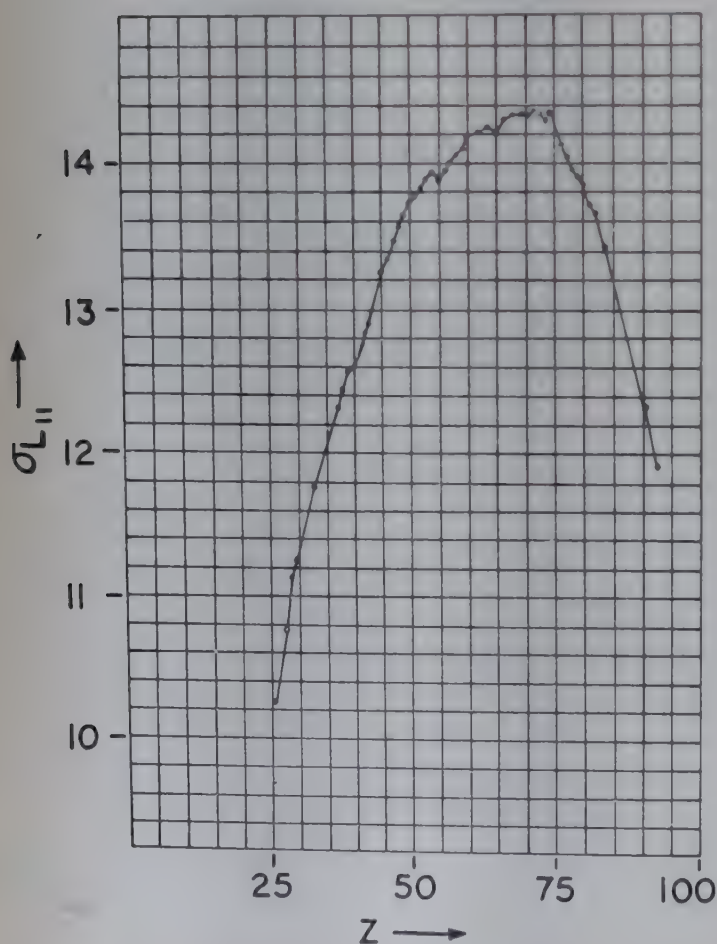


FIG. 2 — Showing the relation between σ_{L_1} and Z .

plotted against the atomic number in curve (2). A few other ν_L -values for elements below 26 Fe may be calculated roughly by a number of indirect methods, *e.g.*, from the empirical relation given by Hertz and Sommerfeld:

$$\sqrt{L_{11}} - \sqrt{L_{21}} = \text{const.} = .64, \quad \dots \quad (6)$$

as has been done by Stoner⁹.

But there is no certainty that the relation⁶ holds for elements below Fe. We can also try to identify ν_{L_1} with some of the critical potentials found by the electron bombardment method. But these values are also uncertain.

Anyhow the values of L_1 below Fe are only provisionally given.

TABLE 4

Z	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{L_1}}{R}}$	σ_{L_1}	Remarks
5 B	1.82	1.35	2.30	Electron bombardment method
6 C	..	1.61	2.78	
8 O	3.69	1.92	4.16	"
9 F	4.67	2.16	4.68	
13 Al	7.41	2.9	7.20	Lindh
14 Si	10.76	3.28	7.44	
23 V	43.43	6.59	9.82	Thoræus' measurements of $L\beta_3$
26 Fe	62.13	7.882	10.24	
27 Co	..	..	..	"
28 Ni	74.29	8.62	10.76	
29 Cu	80.86	8.994	11.112	"
30 Zn	88.19	9.391	11.218	
31 Ga	..	..	..	"
32 Ge	..	..	..	
33 As	112.7	10.62	11.76	"
34 Se	..	..	..	
35 Br	..	..	..	Lindh
36 Kr	..	..	..	
37 Rb	152.25	12.34	12.32	"
38 Sr	163.57	12.79	12.42	
39 Y	174.52	13.21	12.58	"
40 Zr	187.60	13.70	12.60	
41 Nb	199.33	14.12	12.76	"
42 Mo	212.43	14.58	12.84	
43	..	..	..	"
44 Ru	..	..	..	
45 Rh	251.83	15.87	13.26	"
46 Pd	266.41	16.32	13.36	
47 Ag	280.62	16.76	13.48	"
48 Cd	296.13	17.21	13.58	
49 In	312.14	17.67	13.66	"
50 Sn	329.03	18.14	13.72	
51 Sb	346.3	18.61	13.78	"
52 Te	363.9	19.08	13.84	
53 I	382.3	19.55	13.90	"
54 Xe	401.02	20.03	13.94	
55 Cs	422.5	20.56	13.88	"
56 Ba	441.7	21.02	13.96	
57 La	462.3	21.50	14.00	"
58 Ce	482.9	21.97	14.06	
59 Pr	504.0	22.45	14.10	"
60 Nd	524.9	22.91	14.18	
62 Sm	571.2	23.90	14.2	"
63 Eu	594.3	24.38	14.24	
64 Gd	619.9	24.89	14.22	"
65	..	..	..	
66 Dy	667.68	25.84	14.32	"
67 Ho	..	..	..	

TABLE 4 (contd.)

Z	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{L_{11}}}{R}}$	$\sigma_{L_{11}}$	Remarks
68 Er	719.78	26.83	14.34	
69 Tu	747.19	27.33	14.34	
70 Yb	774.55	27.83	14.34	
71 Lu	802.05	28.32	14.36	
72 Hf	830.70	28.82	14.36	
73 Ta	861.3	29.35	14.3	
74 W	889.9	29.83	14.34	
75	..	..	..	
76 Os	957.7	30.94	14.12	
77 Ir	991.0	31.47	14.06	
78 Pt	1022	32.02	13.96	
79 Au	1058	32.54	13.92	
80 Hg	1093	33.06	13.88	
81 Tl	1131	33.64	13.72	
82 Pb	1168	34.17	13.66	
83 Bi	1205	34.78	13.44	
84 Po	..	..	..	
85	..	..	..	
86 Niton	..	..	..	
87	..	..	..	
88 Ra	..	..	..	
89	..	..	..	
90 Th	1508	38.83	12.34	
91 U _{rl}	..	..	..	
92 U _r	1603	40.04	11.92	

The problem of determining ν_{L_1} may be started from that of Beryllium like atoms. We have therefore added in Table 5 the experimentally determined values of the I.P. of atoms stripped to the Be-shell, viz., of Be, B⁺, C⁺⁺. The corresponding screening constants are shown in column 4. It is found that σ_L -values tend to the limit 2.34 for N⁺⁺. It is found that the I.P. of atoms stripped to the Be-core can be represented by the formula

$$E = (Z - 2.34)^2 + 4.27 - \frac{2.61}{(Z - 2.34)} + \frac{3.25}{(Z - 2.34)^2} \dots (7)$$

TABLE 5

Element	I. P. of Stripped atom.	$\frac{\nu}{R}$	σ	σ_{L_1}
Be	9.49	.701	2.320	..
B ⁺	24.19	1.39	2.326	2.78
C ⁺⁺	45.49	3.359	2.334	..
N ⁺⁺	73.46	5.425	2.342	4.16
O ⁺⁺	*[109.26]	8.07	2.342	..

*Approximate.

6. The $\sigma_{L_{11}}$ -absorption levels.— The L_{21} and L_{22} absorption levels are given by Lindh up to 12 Mg. The

values of $\sigma_{L_{11}}$ calculated according to the formula $\sqrt{\frac{\nu_{L_{11}}}{R}} = \frac{Z - \sigma_{L_{11}}}{2}$ are shown in column 4 of Table 6, and the variation of $\sigma_{L_{11}}$ values with the atomic number is shown in curve (3).

TABLE 6

Z	$\frac{\nu}{R}$	$\sqrt{\frac{\nu}{R}}$	σ	Z	$\frac{\nu}{R}$	$\sqrt{\frac{\nu}{R}}$	σ
10 Ne	1.59	1.26	7.48	54 Xe	375.74	19.38	15.24
12 Mg	3.50	1.87	8.26	55 Cs	396.4	19.91	15.18
13 Al	5.20	2.28	8.44	56 Ba	414.67	20.36	15.28
15 P	9.92	3.15	8.70	57 La	434.4	20.84	15.32
16 S	11.68	3.42	9.16	58 Ce	454.44	21.32	15.36
17 Cl	14.81	3.85	9.38	59 Pr	474.68	21.79	15.42
19 K	21.43	4.63	9.74	60 Nd	495.90	22.27	15.46
20 Ca	25.42	5.09	9.82	62 Sm	538.9	23.21	15.58
21 Sc	30.35	5.51	9.98	63 Eu	561.5	23.70	15.6
22 Ti	32.6	5.71	10.58	64 Gd	584.66	24.18	15.64
23 V	38.3	6.18	10.64	66 Dy	632.22	25.14	15.72
24 Cr	43.3	6.57	10.86	68 Er	682.62	26.13	15.74
25 Mn	48.2	6.94	11.12	69	709.23	26.63	15.74
26 Fe	53.42	7.31	11.38	70 Yb	733.70	27.09	15.82
27 Co	59.00	7.68	11.64	71 Lu	762.87	27.62	15.76
28 Ni	64.10	8.04	11.92	72 Hf	791.37	28.13	15.74
29 Cu	70.4	8.39	12.22	73 Ta	819.6	28.63	15.74
30 Zn	77.1	8.78	12.44	74 W	849.59	29.15	15.70
33 As	101.00	10.01	12.98	76 Os	912.6	30.21	15.58
34 Se	108	10.41	13.18	77 Ir	944.3	30.73	15.54
35 Br	117.1	10.85	13.4	78 Pt	977.6	31.27	15.46
37 Rb	137	11.71	13.58	79 Au	1011.3	31.83	15.34
38 Sr	147.88	12.16	13.68	80 Hg	1047.4	32.36	15.28
39 Y	158.84	12.60	13.80	81 Tl	1082.9	32.91	15.18
40 Zr	169.83	13.03	13.94	82 Pb	1120.5	33.47	15.06
42 Mo	193.39	13.91	14.18	83 Bi	1157.5	34.02	14.96
44 Ru	218.57	14.78	14.44	84	..	..	..
45 Rh	231.64	15.22	14.56	85	..	..	..
46 Pd	245.28	15.66	14.68	86	..	..	..
47 Ag	259.87	16.09	14.82	87	..	..	..
48 Cd	274.55	16.57	14.86	88	..	..	..
49 In	290.26	17.04	14.92	89	..	..	..
50 Sn	306.59	17.51	14.98	90 Th	1449.7	38.07	13.86
51 Sb	322.9	17.97	15.06	91	..	..	..
52 Te	340.1	18.44	15.12	92 Mr	1539.8	39.24	13.52
53 I	357.77	18.91	15.18				

The starting point for the calculation of the $\sigma_{L_{11}}$ -values should be the Neon-atom. This has not yet been attempted. In Table 7 we have given the I.P. of atoms ionised to the Ne-like core as far as known, and the calculated values of screening constants are shown in column 4. It is seen at once that $\sigma_{L_{11}}$ tends in the limit to σ_L for Ne. The $\sigma_{L_{11}}$ -values are roughly represented by the empirical formula

$$\sigma = 7.728 + 2.77(Z - 10) - 0.0231(Z - 10)^2 - 0.00001(Z - 10)^3, \dots (8)$$

the I.P. of atoms stripped to the Ne-core can be represented by the empirical formula

$$E = (Z - 6.745)^2 + 1.917 - \frac{42.8}{(Z - 6.745)} \times \frac{70.165}{(Z - 6.745)^2}, (9)$$

The value of the electron-affinity of fluorine calculated from this formula comes out to be 7.10 volts, which is in

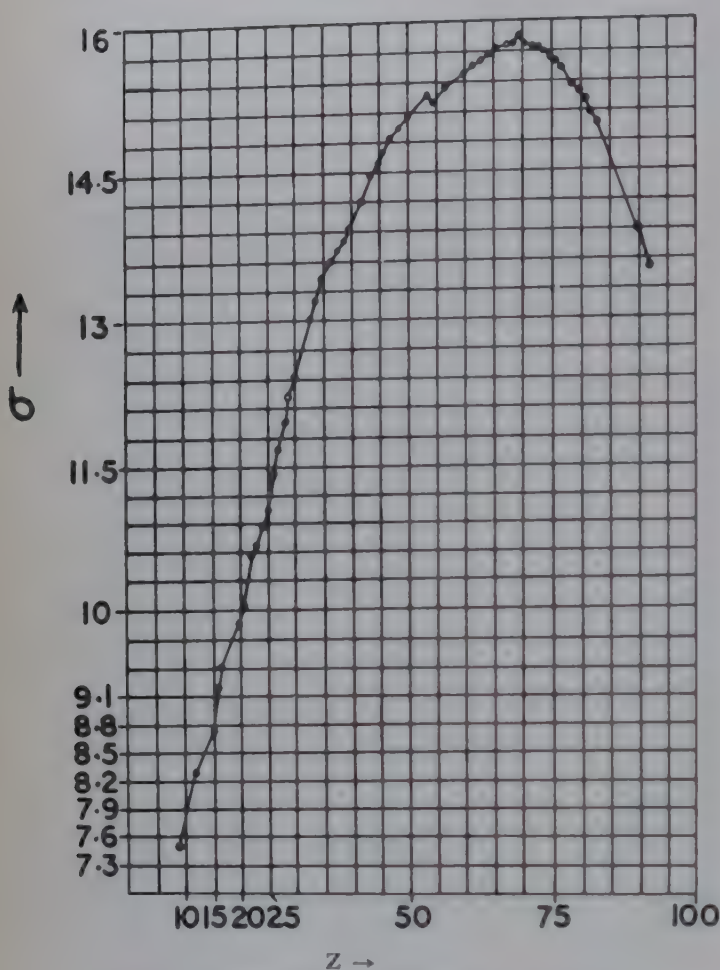
$\sigma_{L_{21}}$ -CurveFig. 3—Showing the relation between $\sigma_{L_{21}}$ and Z .

TABLE 7

Element	I. P. of Stripped atom.	ν/R	σ	$\frac{\nu}{R}$	$\sigma_{L_{21}}$
Ne	21.49	1.59	7.48	1.59	7.48
Na ⁺⁺	46.78	..	7.28	..	..
Mg ⁺⁺	80.91	5.975	7.112	3.5	8.26
Al ⁺	121.77	8.993	7.018	5.2	8.44
Si ⁺	168.72	12.473	6.940	..	..
P ⁺	221.9	..	..	9.92	8.70

agreement with the value got by Mulliken from extrapolation of corresponding values for Cl, Br, I. The formula is similar to Hylleras' formula for He-like stripped atoms, but it has still to be justified on theoretical grounds.

7. *The Probable Cause of Negative Screening.*—It is seen that in all cases, the screening factor shows a negative term involving Z^2 . This reduces the screening constant

ultimately to almost zero in the case of Ur. As far as we are aware, no explanation has yet been given of this negative screening.

A term $-\alpha Z^2$ in the screening factor, is due to a term involving Z^2 in the energy-value of the electron; the power four of Z at once suggests that this factor is due to some polarisation effect, and the only explanation we can give is that the K-electrons produce a polarisation of the nucleus. Further thoughts and actual calculation do not, however, encourage the idea. Firstly, the K-shell is He-like, hence the distribution of charge is spherical, and no polarisation of the nucleus is expected. Secondly, supposing there is a polarisation $=\alpha E$, where E =field produced by the disturbing cause (here the K-electrons), α must be identified with b , b =the radius of the nucleus. But on actually calculating b from the αZ^2 -term, we find that b is about 6×10^{-11} , i.e., b is about sixty times larger than the radius usually ascribed to the nucleus. The explanation therefore seems to fail, and we are not in a position to offer any alternative suggestion.

8. This paper is rather in the nature of a survey of the existing problems. The problems suggested which may be taken up later are:—

(1) To calculate a theoretical expression for the Ionisation Potential of atoms stripped to the Be-core.

(2) To calculate a theoretical expression for the Ionisation Potential of Ne-like atoms.

(3) To find a theoretical expression for the screening effect of outer electrons in the general case.

(4) To find an expression for the potential inside the atom.

(5) To find an expression for the negative squared terms in the screening constant.

(6) To find an expression for the doublet separations.

(7) To calculate energy-values for removing two electrons out of the atoms simultaneously.

(8) To extend the same treatment to the other X-ray levels.

REFERENCES

¹ For example, See Pauling and Goudsmit, *Structure of Line Spectra*, 180.

² M. N. Saha, and B. B. Ray, *Phys. Zeits*, **28**, 221, 1927.

³ See, A Sommerfeld, *Atombau*, Fourth edition, p. 447. Sommerfeld calculates the screening constant from the doublet separations. The method followed here was originally given by G. Hertz, see Siegbahn, *the Spectroscopy of X-rays*, p. 171.

⁴ Thibaud, *Nature*, **121**, 321, 1928.

⁵ M. Söderman, *Phil. Mag.*, **1**, 1931.

⁶ E. A. Hylleras, *Zeits. f. Physik*, **54**, 737, 1929; **65**, 209, 1931.

⁷ B. Edlen, *Zeits. f. Physik*, **59**, 674, 1929; Söderman, *Phil. Mag.*, **10**, (1930).

⁸ Fermi, *Zeits. f. Physik*, **48**, 72, 1928; **49**, 550, 1928.

⁹ A. E. Stoner, *Phil. Mag.*, **2**, 97, 1926.

¹⁰ Lindh, *Handbuch der Experimental Physik*, XXIV, Part 2, 202

54. COMPLEX X-RAY CHARACTERISTIC SPECTRA

M. N. SAHA, SALIGRAM BHARGAVA AND J. B. MUKERJI

(*Nature*, **129**, 435, 1932)

It is well known that for the excitation of the characteristic X-ray spectra of elements, an electron has first to be removed from some internal level; when this is done, an electron from an outer level jumps to this vacant place, and characteristic radiation is emitted. The spectrum is called $K, L, M, \dots$ according to the level of the atom from which the electron was first removed.

This explanation suffices for the origin of the diagram lines, which show the same structure as lines due to alkalis, but there are, besides, other lines, the origin of which is still a matter of debate. Some of these have been traced to forbidden transitions;¹ but in addition, there are the so-called spark lines, which appear as faint satellites to the diagram lines. Hypotheses² have been advanced which ascribe these to double ionisation and single transition.

In this note we wish to direct attention to the existence of a third class of characteristic lines, which are due to *double ionisation and double transition*. Suppose in one single act of bombardment of the anticathode by electrons, two electrons are removed simultaneously from an internal level, say one from L_1 , the other from L_2 , and these places are filled up by simultaneous passage of electrons from higher levels, say one from M_1 , the other from M_3 . It can be shown from quantum principles and from analogy with optical spectra that one of the transitions will be allowed, the other forbidden, so that in the above example the transition may be written as $(L_1 L_2 \leftarrow M_1 M_3)$; it is a composite transition and is the sum of the two transitions (1) $L_2 \leftarrow M_3$, which is allowed, and (2) $L_1 \leftarrow M_1$, which is forbidden. Lines due to such transitions are quite common in optical spectra: for example, in the case of Ba $6s^2 \ ^1S_0 - 5d. 6p. \ ^1P_1 \ \lambda 3501.1$ cited by Russell and Saunders³ in their classical paper on the spectra of alkaline earths.

There is no reason why double transitions should not occur in the X-ray region. But *their frequency will be approximately double the frequency of the usual L -lines*, and since the electron configuration in this case is $2s. 2p^5 \leftarrow 3s. 3d^9$, the lines will form a multiplet $(^1P, ^3P) \leftarrow (^1D, ^3D)$, provided Russell-Saunders coupling continues to hold in such cases. *The fact that their frequency will be double the usual L -spectrum frequency marks them out as a distinct class.*

Attempts have been made in this laboratory to obtain such lines from a tungsten anticathode, and two lines have

been obtained with the wave-lengths $\lambda = 723$ and 682 X.U. They are diffuse lines impressed on a continuous background, and may be found to be attended with satellites when higher resolution is used. These wave-lengths are approximately half the wave-length of tungsten L -lines. After searching the literature to determine whether such lines have been noticed by any previous worker, we find that Rogers⁴ noted in 1923 the following lines from tungsten: $\lambda = 1450, 1373, 1321, 1248.7, 1230, 1114, 1086$ X.U. These have not been traced to the tungsten levels, or identified as satellites or nondiagram lines, and cannot be ascribed to any other element. But it will be seen that the wave-lengths of the first two of Rogers' lines are very nearly double the wave-length of the lines obtained by us. Hence it may be safely concluded that the lines obtained by Rogers are the same double transition lines obtained in the second order.

The full multiplet will be dispersed over a large wave-length range, and, with our present apparatus, such long exposures (amounting to a hundred hours) are needed that considerable time must elapse before the whole set of lines can be photographed. But the fact that double L -frequency lines have been obtained at all indicates that the ideas presented here are essentially sound.

We think that we have established the possibility of getting double transition lines constituting complex spectra in the X-ray region. To get double transition or multiple transition lines due to all elements will be a vast programme, but when this is done, it will probably afford us very useful material for working out coupling problems inside the atom. The idea probably explains the numerous critical levels obtained by Richardson and his students: for the most part, these levels have no apparent connexion⁵ with the recognised X-ray levels which give rise to the diagram lines. This fact is at present inexplicable; but supposing the quantum theory can be adopted to explain the fact, then combining this with the ideas presented here, we find that we get an unforced explanation of the numerous levels obtained by Richardson, and need not give up the Bohr-Stoner levels (cf. Richardson⁶). The J -phenomenon also does not appear to be so inconceivable, as according to our views we may have characteristic

lines approximately double the frequency of ordinary K -lines.*

Department of Physics,
University of Allahabad, Feb. 5.

*The following cablegram dated Feb. 29 has been received from Prof. Saha:

Double transition K -line approximately double frequency K -alpha three obtained copper.—SAHA.

REFERENCES

- ¹ S. Idej, *Sci. Reports Tôhoku Imp. Univ.*, **19**, 560.
- ² B. B. Ray, *Phil. Mag.*, **8**, 772, 1929; Langer, *Phys. Rev.*, **37**, 457, 1931.
- ³ Russell and Saunders, *Astro. J.*, **61**, 38.
- ⁴ Lindh, "Handbuch d. Experimentalphysik", xxiv/2, p. 172.
- ⁵ Chalklin, *Sci. Prog.*, Jan. 1932, p. 437.
- ⁶ Richardson, *Proc. Roy. Soc., A*, **128**, 63, 1930.

55. ON THE β -RAY ACTIVITY OF RADIOACTIVE BODIES

(Preliminary Communication)

M. N. SAHA AND D. S. KOTHARI

(*Bull. Acad. Sci., (Allahabad)* **5**, 257, 1934)

Received on November 6, 1933

INTRODUCTION

The β -ray activity of radioactive bodies has up till now proved to be a baffling problem. The points at issue are summarised in Gamow's *Constitution of Atomic Nuclei*, pp. 52-54, and in *Radiations from Radioactive Bodies* by Rutherford, Chadwick and Ellis. They are also discussed at some length by Bohr in his *Faraday Lecture* (Feb. 1932). We shall later quote freely from Bohr, but some fundamental difficulties may be pointed out at the outset.

The older view of the constitution of the nucleus was that it should be regarded as composed of A protons (A =mass number) and $A-Z$ electrons (Z =nuclear charge). A large number of these protons and electrons may exist in the compound form of α particles ($4p+2e$) or some other composite structures. But even allowing for these, the existence of a number of free electrons had to be postulated inside the nucleus. On the other hand, the evidence of hyperfine structure, as was first pointed out by de Kronig, definitely proves that the electron cannot exist in the free state in the nucleus, for then the magnetic moment of the nucleus should have the magnitude of the Bohr magneton, while the hyperfine structure of spectral lines definitely shows that the moment has the magnitude of the protonmagnet ($\frac{1}{1836}$ times the Bohr-magneton). At the present time, it is almost universally held that the nucleus consists of Z protons, and $A-Z$ neutrons, but it is quite possible that a number of these are combined in the form of α -particles, deutons, etc. *The nucleus contains no electrons free or bound.*^{1,2}

But this conclusion is seemingly at variance with the observed fact that in a β -ray disintegrations the nuclei are observed to eject high speed electrons spontaneously.

The situation is therefore paradoxical. Bohr puts it as follows:—

"Strictly speaking, we are not even justified in saying that a nucleus contains a definite number of electrons, but only that the negative electrification is equal to a whole number of units and in this sense, the expulsion of a β -ray from a nucleus may be regarded as the creation of an electron as a mechanical entity".

In a later passage, Bohr describes the other difficulties as follows:—

"As regards this last question, much theoretical interest has recently been aroused by the peculiar features exhibited by the β -ray expulsions. On the one hand, the parent elements have a definite rate of decay, expressed by a simple probability law, just as in the case of the α -ray disintegrations. On the other hand, the energy liberated in a single β -ray disintegration is found to vary within a wide continuous range, whereas the energy emitted in an α -ray disintegration, when due account is taken of the accompanying electromagnetic radiation and the mechanical energy conversion, appears to be the same for all atoms of the same element".

To the above remarks of Bohr, the following may be added:—

(a) The β -ray disintegration has been observed not only in the case of heavy elements, but also in the light elements potassium and rubidium (or rather the isotopes K^{41} and Rb^{87}). In the case of β -ray bodies associated with the main groups (U, Th, Ac), the life of β -ray bodies is found to vary from 16 years (RaD) to a few minutes, but the light elements K^{41} and Rb^{87} possess lives comparable

with those of some long-lived heavy radioactive bodies. The life of K^{41} has been estimated to be 7.5×10^{10} years, that of Rb^{87} to be 10^{11} years.³ It is quite possible that there may be a number of β -ray elements possessing longer lives which are still undiscovered, as the activity of such bodies is likely to be extremely feeble, and difficult of detection. In support of our view, we may cite the case of Ac , $RaD \dots$ which were long regarded as undergoing rayless changes. They are not actually rayless, but the β -rays are exceedingly feeble, on account of the long life of these bodies.

From these remarks it will be clear that there is no essential difference between the orders of ranges of the lives of β -ray and α -ray bodies.

(b) Ellis⁴ has shown in numerous papers that one β -particle is emitted per one disintegrating atom, so that the possibility that the expulsions are due to some external agency seems to be ruled out. They are spontaneous processes like α -ray disintegration.

(c) The distribution of energy in the β -ray spectrum—This point has formed the subject of investigation by a large number of workers. The curves bear some resemblance to Planck's curve for blackbody radiation but unlike that curve, it has got a limit on the high energy side and the maximum is ill-defined. They also present some similarity to the curves obtained by Kuhlenskampf on the distribution of intensity in the continuous X-ray spectrum.

There has been an idea that the β -rays are probably emitted with quite a definite energy from the nucleus, but in its passage through the outer shell of electron, it suffers diminution in energy owing to collision or scattering but this view has been disproved by Ellis⁵. Lately, attempts have been made to determine the maximum energy as accurately as possible and to deduce from it a relation similar to that of Geiger and Nutall for α -ray bodies.

The latest exponent of this idea is Sargent⁶ who found in a recent paper that every β -ray disintegrating atom is distinguished by having a definite end-point in its energy-spectrum. But a reference to his figures shown in Table VI, p. 670, and his curves on p. 671, Fig. 2, shows that there is not much evidence of a relation. For the points lie on three distinct curves, and the radioactive bodies belonging to the same family do not lie on the same curve. Secondly, if the Geiger-Nutall law for α -ray bodies is expressed in the form $\lambda = aE^n$ where E = energy of the α -particle varying between 4 to 8 million electron-volts, λ varies from 10^5 sec^{-1} (Th C') to $10^{-18} \text{ sec}^{-1}$ (U), n is found to vary from 65 to 100. But for the β -ray bodies, E varies from $3.5 \times 10^4 \text{ evs}$ to $3.15 \times 10^6 \text{ evs}$, i.e., a range of about 1 to 100, but λ varies from 10^{-2} sec^{-1} to 10^{-9} sec^{-1} and if λ be put $= bE^n$, n varies from 3 to 7. The attempt to trace a causal connection between the decay constant and the maximum β -ray energy does not appear to have been successful. We shall see later that no such causal connection is expected.

The fact that the β -ray bodies follow the same law of decay as α -ray bodies can, however, point to only one conclusion, i.e., the phenomenon is due to the leakage of α -rays through a potential barrier, but somehow the α -ray does not leave the nucleus, but a γ -ray is generated in its place.

Bohr weighs the probability that the continuous β -ray energy spectrum may be due to differences in the energy contents of the individual parent atoms leading to small and undetectable differences in their mass, but finally decides against this view. The following are his words.

"Unless the expulsion of β -rays from atomic nuclei, contrary to expectation, is not a spontaneous process but caused by some external agency, the application of the principle of energy conservation to β -ray disintegration would accordingly imply that the atoms of any given radio element would have different energy contents. Although the corresponding variations in mass would be far too small to be detected by the present experimental methods, such definite energy differences between the individual atoms would be very difficult to reconcile with other atomic properties. In the first place, we find no analogy to such variations in the domain of non-radioactive elements. In fact, as far as the investigations of nuclear statistics go, the nuclei of any type, which have the same charge and within the limits of experimental accuracy, the same mass, are found to obey definite statistics in the quantum mechanical sense, meaning that such nuclei are not to be regarded as approximately equal, but as essentially identical. This conclusion is the more important for our argument, because in absence of any theory of the intra-nuclear electrons, the identity under consideration is in no way a consequence of quantum mechanics, like the identity of the extra-nuclear electronic configurations of all atoms of an element in a given stationary state, but represents a new fundamental feature of atomic stability. Secondly, no evidence of an energy variation of the kind in question can be found in the study of the stationary states of the radioactive nuclei involved in the emission of σ and γ rays from members of a radioactive family proceeding or following a β -ray product. Finally, the definite rate of decay which is a common feature of α - and β -ray disintegrations points even for a β -ray product, to an essential similarity of all the parent atoms, in spite of the variation of the energy liberated by the expulsion of the β -ray. In absence of a general consistent theory embracing the relationship between the intrinsic stability of electrons and protons and the existence of the elementary quanta of electricity and action, it is very difficult to arrive at a definite conclusion in this matter."

We have quoted this passage in full, because after this paper was written, we came across a paper by Beck⁷ where this idea of hypothetical differences in the energy contents of the individual parent atoms resulting in small and undetectable differences in their mass has been revived

to account for the continuous energy distribution amongst the ejected β -rays.

Finally, in order to explain events, Bohr wants to sacrifice the law of conservation of energy and suggests the following process :

"At the present stage of atomic theory, however, we may say that we have no argument, either empirical or theoretical, for upholding the energy principle in the case of β -ray disintegrations, and are even led to complications and difficulties in trying to do so. Of course, a radical departure from this principle would imply strange consequences, in case such a process could be reversed. Indeed if, in a collision process, an electron could attach itself to a nucleus with loss of its mechanical individuality, and subsequently be recreated as a β -ray, we should find that the energy of this β -ray would generally differ from that of the original electron. Still just as the account of those aspects of atomic constitution essential for the explanation of the ordinary physical and chemical properties of matter implies a renunciation of the classical ideal of causality, the features of atomic stability, still deeper-lying responsible for the existence and the properties of atomic nuclei, may force us to renounce the very idea of energy balance."

The above short summary will probably convey some idea regarding the complexity of the problem.

2. ELECTROFISSION OF LIGHT QUANTA

It appears that the β -ray disintegration admits of a rather simple interpretation on the basis of the recent experiments by Anderson and Neddermeyer⁸, Meitner and Hupfeld⁹, Curie and Joliot¹⁰ on the production of pairs of positrons and electrons by impact of hard γ -rays with atomic nuclei. As the description of this fundamental discovery, which promises to throw a flood of light on nuclear physics, is still scattered over the pages of many scientific journals, we try to give a connected account of it here. Skobelzyn¹¹ was the first to use vertical Wilson Chambers placed within a horizontal magnetic field for photographing the track of cosmic rays. He found that the cosmic rays gave rise to tracks of β -rays possessing extremely high energy. In some cases, the mass-equivalent of the energy was as great as 50-100 times the rest-mass of the electron. On repeating these experiments, Anderson⁸ found that in addition to the tracks due to high energy β -rays there were others possessing equal curvature, but bent in the opposite direction. From the nature of ionisation along these tracks, it was clear that they were due to particles of the same type as electrons, but possessing an opposite, *i.e.*, a plus charge. To this particle, which is the exact positive analogue of the electron, the name *positron* was given. Subsequently Meitner and Hupfeld⁹ obtained similar paired tracks of electrons and positrons by taking Wilson photographs of Be-radiations impinging on Pb

and Anderson and Neddermeyer and Curie and Joliot¹⁰ showed that even the hard γ -rays from ThC^{*} having the energy 2.6 *mevs* can give rise to such paired tracks (*mevs* stands for million electron volts).

HOW ARE THE PAIR POSITRON AND ELECTRON PRODUCED?

Anderson and Neddermeyer, and Blackett and Occhialini¹² further showed that this production of "paired ions" accounts for a number of unexplained facts. Gray and Tarrant¹³ had previously shown that hard γ -rays show an anomalous absorption which is not accounted for by the Klein-Nishina formula for scattering. The anomalous absorption was found by them to start at the γ -ray energy 2 to 3 *mevs*. Later Gentner¹³ fixed the limit at 1.2 *mevs*. We have to remember in this connection that m_0c^2 , the rest energy of the electron corresponds to 5×10^5 *evs* and thus the energy of a pair of electron and positron at rest is equivalent to 1 *mevs*. Hence there is a connection between the beginning of anomalous absorption, and the production of "paired ions." Blackett and Occhialini¹¹ suggested that within the nucleus, the γ -ray is split up, under the intense electric field, into a pair consisting of a positron and an electron. Oppenheimer and Plessett¹⁴ regarded the phenomenon as a photo-electric effect, the γ -ray quantum lifting an electron occupying one of Dirac's negative energy states into a positive energy state, thus simultaneously creating an ordinary electron and a "hole" which according to the ideas of Dirac will correspond to the positron (*vide* § 3). Curie and Joliot¹⁰ have proposed to denote this phenomenon as "*materialisation of quanta*."

Blackett further showed that the hypothesis of the splitting of the quantum inside the nucleus explains another interesting observation by Gray¹² and others. The former has subjected the nuclei of many atoms to hard γ -rays from ThC^{*} and found that the nuclei were thereby excited to a fluorescent radiation of approximate wavelengths 12X. units and 24X. units. The first possesses an energy of 1 *mevs* and the second $\frac{1}{2}$ *mevs*. According to Blackett, though the γ -ray may split up inside the nucleus into a pair of positrons and electrons, but the two may again combine either inside the nucleus or just outside. When they combine inside the nucleus only one quantum of energy 1 *mevs* units may be produced. If they combine outside, two quanta each of energy 0.5 *mevs* units will be produced.

We are of opinion that the phenomenon of conversion of a γ -ray into a pair of ions of opposite sign, confirmed by so many investigators in different parts of the world, should be designated by a more expressive term than Curie and Joliot's *Materialisation of Quanta* and the round-about phraseology about holes, etc., borrowed from Dirac's theory should be avoided, and we have ventured to suggest the term '*Electrofission of Light Quantum*...' which clearly

expresses the idea that under the influence of the nuclear fields, the quantum of energy undergoes a 'fission' into elementary charges of opposite sign, the balance of energy being distributed as kinetic energy amongst the two products in a way which is still to be determined. The possibility of the reverse process of two charges neutralising each other in a direct collision has been postulated by many astrophysicists in a slightly different form. But when these predictions were made, the positive unit of electricity was known to be always associated with the mass in a proton, and nobody could conceive of a positron, hence they always talked of annihilation of proton and electron, but the hypothesis has always lacked vigour on account of want of experimental proof. The process as now actually found is different from the early hypothesis about annihilation in many other points.

THEORETICAL PREDICTIONS ABOUT POSITRON

It may be added at this stage that grounds for the advent of the positron were to some extent prepared by the predictions of Dirac¹⁵ from his relativistic theory of the electron. In this he was first led to postulate the existence of an elementary particle having the charge- e but possessing the negative energy— mc^2 . Such a particle (the anti-electron) would possess very weird properties which have not been observed. We quote from Gamow

"For such particles the force and acceleration are directed in opposite directions. If two electrons, one of 'positive' and the other of 'negative' mass, meet then the first will be repelled and the second attracted to the other one; both electrons will fly away one behind the other with infinitely increasing velocity, giving an amusing picture of electronic races."

Later, Dirac developed a theory of 'holes' to account for 'positive charges'. He postulated that in Nature all the negative energy states are usually fully occupied, but sometimes a hole may appear. A positive energy electron will then jump into the hole, resulting in the neutralisation of charges and release of the energy $> 2m_0c^2$ as radiation in the form of one or two quanta. The process is thus equivalent to the so-called annihilation of charges. The 'hole' can be identified as a "unit positive charge". But it could not be identified with the 'proton' because the mass of the proton is 1836 times heavier than that of the 'hole'. The discovery of the positron exactly corresponds to Dirac's hole, but sweeps away the misleading ideas about particles capable of possessing "negative energy-state". These ideas are not a little responsible for creating confusion in contemporary scientific thought. Instead of an anti-electron with a negative energy we have now a straight-forward positive analogue to the electron with positive charge and positive energy.

THE PROTON

The question of the nature of the Proton now becomes a problem. According to one view, the proton is not a fundamental particle but is a compound of the neutron and the positron. If this view be correct, the neutron is merely 'mass' possessing an inherent tendency to capture positrons, but behaving in a different way towards electrons which they cannot capture for if this could take place, we could obtain a negative proton. There is also certain amount of experimental evidence in favour of this view. Anderson and Neddermeyer, as well as Curie and Joliot found in their experiments on *Electrofission* of ThC' γ -ray quantum that more electrons are obtained than positrons, Curie and Joliot¹⁰ give the following figures.

Number of positrons per 100 electrons (Magnetic field 1100 gauss).

Al	Cu	Pb	U
5	18	30	40

But working with cosmic rays which can now be definitely taken to be super γ -rays, it has been found by Anderson as well as Kunze¹⁶ that the number of positron tracks is equal to the number of electron tracks. These results, can be explained on the hypothesis that positrons are easily absorbed by the constituents of the nucleus, possibly neutrons, while electrons are repelled by them. Only very high energy positrons can resist capture by nuclei. Further, if the neutron, the electron and the positron are fundamental particles, they should possess the angular momentum

$\frac{1}{2} \frac{h}{2\pi}$ (and be guided by Fermi-Statistics). The protons

according to this view may have varying angular momentum depending upon the state of the combination between the neutron and the positron, a view which seems to be in agreement with the latest results of Stern and Easternmann.¹⁷ According to Chadwick,¹⁸ however, the proton is probably fundamental, and the neutron is a "dipole" composed of the proton and the electron. As the difference of mass on the two views is of the order of $\cdot 00054$, the question cannot probably be ever determined by a precision estimation of masses, but only by investigation of the response of the neutron to light quanta. For, Chadwick's neutron being a dipole, would be highly reactive towards electromagnetic radiation, while the mere 'mass-neutron' is not expected to be reactive. Even on this point, we are not on very sure grounds, for according to one of us, the neutron is a magnetic dipole, composed of two free Dirac's magnetic poles separated by a distance of $\frac{e^2}{Mc^2}$ which is $\frac{3}{2}$ times the protonic radius, but these views have no effect on the present course of investigation.

Though not directly connected with the subject-matter of this article, it may be pointed out that the two views regarding the proton will have different consequences in

astrophysics. According to many astrophysicists, hydrogen is found in abundance in many stars, and there is a likelihood that the chief constituent of all stellar matter is hydrogen. This must exist in the interior as protons. The proton, if it is a compound will be further broken up into the neutron and the positron, for the binding energy is small, between 10^4 to 10^5 evs, and even the smallest temperature ascribed to stellar interiors is sufficient for the complete breaking of the proton. The other (Chadwick's) view does not allow this breaking, for the proton being fundamental cannot be further subdivided. So on the first view the stellar core will consist of neutrons, positrons and electrons; while on the second view, it will consist of protons and electrons. This is fraught with far-reaching consequences. For the neutrons have been found to possess the remarkable property of passing through matter till they are stopped by the nucleus, and when they strike the nucleus, they excite radical changes in it, resulting in the emission of protons, γ -rays, α -particles. One of us is at present engaged in working out a model of a star whose interior is mainly composed of neutrons.

ANNIHILATION OF CHARGES

In this connection, we may refer to the hypothesis about annihilation of matter advocated by Jeans and Eddington¹⁹ to account for the source of stellar energy. A certain amount of vagueness is always attached to such hypothesis, for annihilation literally means to be reduced to nothing, but the process described here is very different from unalloyed nihilism on the part of fundamental particles, for when an electron and proton hit each other, a neutron and a γ -ray is produced. There is no violation of the principle of conservation of energy or momentum, so nothing is annihilated except that the charges seemingly disappear. The energy of the γ -ray is available for supplying the stellar energy, but it is not yet known whether the mass of the neutron can be converted into energy. Again, when an electron and positron collide outside a nucleus an application of the principle of conservation of energy and linear momentum shows that two quanta must be produced in their place. If they collide inside the nucleus, there may be one quantum as the nucleus can bear certain amount of the shock and thus ensure the obedience to the law of conservation of momentum. In both these processes, there are more variables than equations, and hence the energy of the quanta cannot be uniquely determined. In none of these processes of collision there is either annihilation of mass, or energy, and not even of charges, for in the quantum formed, the two charges probably retain their individual existence as components of a dipole moving with the velocity of light, and they can again be separated when a "fission" takes place. This picture is very different from what is conveyed by Eddington's picturesque description

of the phenomenon as a "joint suicide of the electron and the proton."

3. EXPLANATION OF β -RAY ACTIVITY

We shall now discuss how the β -ray activity can be explained. It is clear that if a γ -ray or supergamma (cosmic) ray coming from outside can split up inside the nucleus into an electron and a positron, it will be much more easier for a γ -ray, of sufficient energy, which is produced within the nucleus to undergo spontaneously such a process of electrofission. Of the pair produced, the electron will be ejected as a β -ray, but the positron cannot usually escape, for it will be prevented by the potential barrier from escaping when such barriers exist, or attach itself to some neutron which is present inside the nucleus. For we have already seen that the neutron has an affinity for the positron, but none for the electron. The net charge in any case will be increased by unity, as is observed in β -ray disintegration. It attaches itself to a neutron, γ -rays of small energy of the order of .05 mevs would probably be given off, which are always observed in a β -ray disintegration. It is not difficult to account for the continuous distribution of β -ray energy, for the primary γ -ray while undergoing '*Internal electrofission*' may have its energy divided between the pairs within wide limits and a certain amount of energy will be communicated to the nucleus. But exact mathematical calculations can be carried out only when more data are forthcoming. The problem of annihilation of two charges of opposite sign which is the converse of the present problem has been discussed by Dirac²⁰, Tamm, and Oppenheimer on the basis of Dirac's holes as positrons.

According to the above view, the β -ray emission is only a secondary process, the primary phenomenon which starts the chain of events which we call a β -ray disintegration is the generation of primary γ -ray within the nucleus. We may now ask ourselves: how is this γ -ray generated? For this, a discussion of the recent theories of a α -ray disintegration is necessary.

It is now well known that classical mechanics offered no solution to the problems of radioactivity. Gamow, and Gurney and Condon first suggested methods for explaining many features of radioactivity from the standpoint of wave-mechanics. The methods were elaborated in great detail by Gamow who succeeded in achieving a good deal of success in explaining the essential features of α -ray disintegration and γ -ray origins. Very substantial contributions were also made by Laue, Fowler, Fowler and Wilson, Atkinson and Houtermans, Schrödinger and others.²¹

All these works suffer from the defect that we have as yet no sure knowledge of the structure of nucleus, *i.e.*, of the constituent particles, the statistics obeyed by them and the laws of interaction towards each other. Hence, as in the earlier stages of study of many other branches or

science, ad hoc hypotheses based on previous knowledge, have to be invented, and the value of these hypotheses is determined by the amount of success achieved by them. It now seems to be fairly certain as mentioned in the introduction that the nucleus consists of protons and neutrons only, and that there are no free electrons (or negative charge in any form) in the nucleus. Most of the protons are combined in the form of α -particles. From a scrutiny of Aston's mass-defect curves it has been deduced that elements after Pb are mostly built up by the addition of only α -particles to the Pb nucleus. Thus U (238/92) the parent of radioactive elements having $A=4n+2$ consists of a Pb nucleus (206/82) with 8 α -particles about it. Th (232/92) the parent of radioactive elements having $A=4n$ consists of the lead nucleus (208/82) with 6 α -particles about it. The mass-defect curve shows that the binding force of these α -particles is very small, *i.e.*, they can be regarded as free to a certain extent. They are prevented from leaving the nucleus by the existence of a potential barrier about the nucleus, whose height is larger than the energy of the α -particles in the crater. According to classical mechanics it will be impossible for the particles to leave the nucleus, but it was suggested by Gamow, and Gurney and Condon that according to wave-mechanics they can be regarded as waves, and thus possess the property of leaking through the barrier. The rate of leakage through the barrier determines the decay of the elements. Various hypotheses have been postulated regarding the height, size and form of the barrier, but the final results agree in their essential features. There is, however, a large amount of divergence in the methods of mathematisation of the ideas. Laue and others take simplified cases²¹, in which the process is regarded as stationary and calculate the rate of leakage through an oblong-shaped potential barrier. Though the mathematics is much simplified, the picture does not evidently correspond to facts as the process cannot be regarded as stationary (independent of time). Gamow,²² on the other hand, introduces complex eigen-values, and by a suitable formulation of boundary conditions, obtains values of decay constants as well as of the eigen-values for the energy of the α -particles inside the crater. His final results are

$$\log \lambda = \log \frac{h}{4\pi r_0^2} - \frac{8\pi^2 e^2 (\mathcal{Z}-2)}{h V_e M} + \frac{16\pi e m^{\frac{1}{2}} (\mathcal{Z}-2)^{\frac{1}{2}}}{h M} r_0^{\frac{1}{2}},$$

$$E = \frac{n^2 h^2}{8\pi r^2} + U_0 = \frac{1}{2} m V_e^2,$$

where e , h and $\mathcal{Z}$ have their usual meaning. M is the mass of the α -particle and V_e is the velocity with which it escapes. r_0 is the "radius" of the product nucleus and V_0 mean potential energy of an α -particle inside it.

It is seen from the above formula that they involve two constants, *viz.*, r_0 the equivalent radius of the crater, and

V_0 the velocity of ejection of the α -particle. According to our picture, r_0 should not much vary for elements belonging to the same radioactive family while the radius v_0 is found to vary in a regular way from U to RaC and from Th to Th A. We get abnormally low values for it when we come to those interesting products RaC, ThC and AcC which disintegrate in a dual fashion, emitting both α - and β -rays. The value of r_0 falls from 8.3×10^{-12} for RaA to 6.3×10^{-12} for RaC; and from 8.1×10^{-12} for ThA to 6.6×10^{-12} for ThC.

We revert again to the question as to how the primary γ -ray referred to above which, by undergoing internal electrofission gives rise to the observed β -decay, is generated. It is reasonable to postulate that there are more than one potential barrier inside a nucleus, though their exact nature (*i.e.*, their height and width) and forms can only be determined when we have a sufficient knowledge of the structural arrangement of the particles constituting the nucleus. Our assumption is that the primary γ -ray is generated by the leakage of an α -particle through an internal potential barrier, *i.e.*, the α -particle leaks from one crater to another, both within the nucleus. It occupies a lower energy level in the new crater and the balance of energy constitutes the primary γ -ray. This primary γ -ray suffers an electrofission producing a positive and a negative electron. The positive electron attaches itself to one of the neutrons present inside the nucleus, thus raising the nuclear charge by unity. The negative electron is ejected, which constitutes the usual β -ray. The combination of the positron with the neutron will liberate some energy (nearly equal to the difference between the masses of positron+neutron, and the proton) and this may account for the soft γ -rays that usually accompany a β -disintegration. The life of the β -decay is determined by the rate of leakage of the α -particle from one inside crater to another and hence to the first order will be independent of the energy of the β -rays. Thus no simple relation (unlike the case of α -decay) is expected to exist between the maximum energy of β -rays and the life of β -decay, a conclusion which is more or less borne out by Sargent's curves.

On the above view it is to be expected that occasionally a positron may not be captured by the neutron, and it may emerge. The presence of positrons associated with the natural β -decay as suggested by Skobelzyn's experiments lends support to the views herein stated.

The explanation of the continuous energy distribution in the β -ray spectrum offers no special difficulties. In our case the energy of the primary γ ray is shared between the positron and the electron, and so the energy of the electron can vary from zero to a maximum ($h\nu = \epsilon + 2m_0 c^2$). The exact form of the distribution curve can only be calculated when we make additional assumptions regarding the mechanism of interaction. This will be examined on a future occasion.

REFERENCES

- ¹ Heisenberg, *Zeits. f. Phys.*, **77**, 1, 1932; **78**, 156, 1932; **80**, 587, 1933.
- ² Lande, *Phys. Rev.*, **43**, 620, 624, 1933.
- ³ Rutherford, etc., Radioactivity, p. 541.
- ⁴ Rutherford, etc., Radioactivity, Chap. XIII.
- ⁵ Ellis and Wooster, *Proc. Roy. Soc.*, **117**, 109, 1927;
- Meitner, *Zeits. f. Phys.*, **60**, 143, 1920.
- ⁶ Sargent, *Proc. Roy. Soc.*, **139**, 659, 1933.
- ⁷ Beck and Sitte, *Zeits. f. Phys.* **86**, 105, 1933.
- ⁸ Anderson and Neddermeyer, *Phys. Rev.*, **43**, 1034, 1933.
- ⁹ Meitner and Hupfeld, *Naturwissensch.*, **21**, 286, 1933.
- ¹⁰ Curie and Joliot, *Jour. de Phys. et Rad.*, **4**, 492, 1933.
- ¹¹ Blackett and Occhialini, *Proc. Roy. Soc.*, **139**, 699, 1933.
- ¹² Gray and Tarrant, *Proc. Roy. Soc.*, **136**, 662, 1932.
- ¹³ Gentner, *Comptes Rendus*, **197**, 403, 1933.
- ¹⁴ Oppenheimer and Plessett, *Phys. Rev.*, **44**, 53, 1933.
- ¹⁵ Dirac, *Proc. Roy. Soc.*, **126**, 360, 1930; **133**, 60, 1931.
- ¹⁶ Kunz, *Zeits. f. Physik.*, **80**, 559, 1933.
- ¹⁷ Eastermann and Stern, *Zeits. f. Phys.*, **85**, 17, 1933.
- ¹⁸ Chadwick, *Proc. Roy. Soc.*, **142**, 1, 1933.
- ¹⁹ Eddington, Internal Constitution of Stars.
- ²⁰ Dirac, *Proc. Camb. Phil. Soc.*, **26**, 361, 1930.
- ²¹ Gamow, *Zeits. f. Phys.*, **51**, 204, 1928;
- Gurney and Condon, *Nature*, **122**, 439, 1928;
- Laue, *Zeits. f. Phys.*, **52**, 726, 1928;
- Houtermans, *Engeb. d. exakt. Naturwissensch.* IX, p. 100, 1930.
- ²² Gamow, Radioactivity, Chap. II.

56 (a). A SUGGESTED EXPLANATION OF BETA-RAY ACTIVITY

M. N. SAHA and D. S. KOTHARI

(Nature, **132**, 747, 1933)

THE β -ray activity of radioactive bodies has until now proved to be a very baffling problem. The points at issue are summarised in Gamow's "Constitution of Atomic Nuclei", etc. (pp. 52-54), and in "Radiations from Radioactive Bodies" by Rutherford, Chadwick and Ellis (p. 385). They are also discussed at some length by Bohr in his Faraday lecture (1930).

Briefly speaking, the chief points under discussion are the following: the disintegration electrons (β -rays) from a radioactive body are not emitted with a single velocity as in the case of α -rays, but show a distribution of velocities over wide ranges, though the breaking-up of the atom is a unitary process, as is proved by the fact that the life-period is definite and there is one electron for each disintegrating atom. It has further been proved that the continuous distribution of velocities is a nuclear process, and not due to action of the surrounding shell of electrons.

It appears that the β -ray disintegration admits of a very simple explanation on the basis of the recent experiments by Anderson and Neddermeyer, and Curie and Joliot on the production of positrons by the impact of hard γ -rays with the nuclei of elements. These experiments have been interpreted by Blackett and Occhialini as indicating the conversion of a γ -ray quantum into an electron and a positron near the nucleus. Curie and Joliot have brought further evidence in favour of this view by showing that γ -rays of thorium C'' (energy 2.6×10^6 electron volts) are converted inside all matter into an electron (mass 9×10^{-28} gm., energy $m_0 c^2 = 0.51 \times 10^6$ eV) and a positron (having the same mass and energy as the electron), the excess energy

being distributed as the kinetic energy of the two particles, and the energy of the residual quantum. They have denoted this phenomenon by the term 'materialisation of light quanta'. They have further shown that a proton is a complex structure, being a compound of the neutron and a positron. As pointed out by Blackett and Occhialini, this explains the anomalous absorption of γ -ray quanta observed by Gray and Tarrant, which Gentner has found to commence with the γ -ray possessing the limiting energy 1.1 million electron volts.

The discovery, which is confirmed by so many workers, promises to be of great importance, as it establishes for the first time, on experimental grounds, the splitting up of a quantum into two charged particles of opposite sign. Many astrophysicists have postulated the probability of the annihilation of the proton and the electron with their mass energies converted into quanta, but the actual process, as revealed by these experiments, seems to be very different. For the quantum breaks up into charged particles possessing opposite charges, but having equal mass, and the positron being absorbed by the neutron forms the proton which is thus seen to be complex. The phenomenon is therefore not a "materialisation of the quantum" as Curie and Joliot suggest, for the neutron appears to be the fundamental mass-particle, but it consists in a splitting of the quantum into two fundamental opposite charges. We may call it 'electro-division of the quantum'.

Let us see how we can explain β -ray activity. If the 'electro-division of a quantum' can be brought about by a nucleus when the quantum hits it from the outside, it is

much more probable that the γ -rays produced within the nucleus itself should be completely split up into an electron and a positron. The electron will come out as a β -ray, but a positron will not be able to come out if the conversion takes place 'within the potential barrier. It will attach itself mainly to some one of the numerous neutrons which are present in the nucleus, and thus form a proton. The positive charge of the nucleus will therefore be increased by unity.

It is not difficult to explain the continuous distribution of β -ray energy. The γ -ray may suffer this 'internal electro-division' anywhere within the nucleus, and hence the velocities imparted to the resulting electrons may vary within wide limits. The exact mathematical calculation can be carried out only when more data are forthcoming. The positron combining with the neutron will give rise to the softer γ -rays which are always present in a β -ray disintegration.

According to the above view, the β -ray emission is only a secondary process, the primary phenomenon which starts

this chain of events being the generation of a primary γ -ray. We can now ask ourselves: How is this γ -ray generated? It must be due to the passage of an α -particle or proton from one barrier to another. Gamow, and also Condon and Gurney have postulated the existence of only one barrier in a radioactive nucleus for explaining the emission of α -rays, with definite velocity, but several lines of argument indicate that there may be more than one barrier present in the nucleus. When an α -particle crosses from one barrier to the other, the γ -ray responsible for the whole chain of events leading to the β -ray disintegration is emitted. The life-period is therefore determined by the time of leakage of an α -particle or proton from one barrier to another, and this explains why the life-periods of β -ray bodies are of the same order as those of α -ray bodies, and have a definite value.

Department of Physics.

Allahabad University. Oct. 20.

56 (b). A SUGGESTED EXPLANATION OF BETA-RAY ACTIVITY

M. N. SAHA AND D. S. KOTHARI

(*Nature*, **133**, 99, 1934)

IN continuation of our letter on the above subject which was published in *NATURE* of November 11, 1933, p. 747, we wish to add the following remarks:—

We have changed the term 'electrodivision of quantum' used in that letter to 'electrofission of quantum'. Under the intense electrical field of the nucleus, a quantum of sufficient energy undergoes *fission* into an electron and a positron, the energy being distributed between them in varying proportions, but the law of conservation of energy continues to hold good.

Our interpretation offers an unforced solution of Bohr's paradox that though the nucleus contains no electrons, free or bound, but only positive particles (α -rays, protons) and neutrons—a view which is now universally held—a β -ray can be created inside it and ejected with high speeds. It has further been established that radioactivity, whether marked by an α -ray or a β -ray disintegration, is mainly due to the leakage of loosely bound α -particles through the potential barrier. The β -ray is only a by-product, when the α -particle cannot escape, but on leaking to the second crater falls into a lower level, and gives rise to a γ -ray which undergoes fission into an electron and a positron.

We should further add that the phenomenon of 'electrofission' is different from the reverse process of annihilation of charges or conversion of radiant energy into mass postulated by many astrophysicists. For when a positron and an electron combine to form one or two γ -ray quanta, the charges do not neutralise but form a dipole which can be again disrupted into its constituents. This does not bring us nearer to the problem of the total conversion of mass to radiation, for the main amount of mass resides in the neutron, which according to one of us (Kothari) is a dipole formed of two Dirac magnetic poles of opposite sign, separated by a distance of e^2/Mc^2 . The neutron evidently cannot be disrupted by the nucleus; the binding is too strong. It may be disrupted, however, by the electromagnetic action of cosmic rays, giving rise to free magnetic poles. Such phenomena, to our knowledge, have not yet been observed.

Much other evidence, physical as well as astrophysical, in favour of these views has been obtained.

Allahabad.

Dec. 5.

57. INNER CONVERSION IN X-RAY SPECTRA

M. N. SAHA AND J. B. MUKHERJEE

(*Nature*, **133**, 377, 1934)

MORE than ten years ago, Coster¹ reported that he had carried out experiments with heavy elements for tracing X-ray characteristic lines due to the transition $L_1(2s) \leftarrow L_{2,3}(2P_{\frac{1}{2}}, 2P_{\frac{3}{2}})$, but got no positive results. During the last ten years, a number of other investigators² have also reported negative results.

These failures have remained rather mysterious for the transition $L_1 \leftarrow L_{2,3}$ ($\Delta n=0$) is not forbidden by quantum mechanics and actual calculation based on wave mechanics shows that the expected line should be quite intense. A recent search by one of us (J. B. M.) for the expected line of W (L_1-L_3 ; $\nu/R=139.5$; $\lambda=6.4\text{\AA}$.) also yielded no positive result though both the excitation and exposure were more than sufficient. A search into the current literature shows that though these lines (L_1-L_3) have not been obtained, a number of lines of heavy elements (73 Ta to 81 Tl) due to the transitions between N -levels ($N_{4,5} \leftarrow N_{6,7}$) have been obtained by Thibaud³, del Rosario⁴, Magnusson⁵, Prins and Takens⁶, while the last two workers report lines due to the transitions ($M_{2,3} \leftarrow M_{4,5}$) of a number of elements. Since in all these lines $\Delta n=0$, the failure to obtain the lines due to the transition ($L_1 \leftarrow L_3$) was remarkable.

It appears to us that the failure to obtain the ($L_1 \leftarrow L_3$) line is to be completely ascribed to the inner conversion of such lines in the M -levels of the elements. A scrutiny of the L -level values of the elements shows that from 92 U to 68 Er the (L_1-L_3) values are greater and very close to

the M -level values; for example, in W, the ν/R value for (L_1-L_3) is equal to 139.5 while $M_4=137.5$, $M_5=132.9$.

An application of a modified form of the formula for inner conversion given by Miss Swirles, Taylor and Mott and Hulme⁷ shows that the (L_1-L_3) lines should be completely converted in such cases. It is only in 68 Er that the (L_1-L_3) ν/R value is just less than any of the M -level values and much larger than N -level values. But this situation persists only up to 55 Cs; from iodine again, L_1-L_3 becomes just larger than some M -values, so that it is expected that only elements from Er to Cs are capable of showing lines due to ($L_1 \leftarrow L_3$) transitions. This conclusion has not yet been tested.

It appears that the phenomenon of inner conversion is responsible for many of the intensity anomalies which are observed in the line spectra of X-rays, as was suggested some years ago by Wentzel.

Physical Laboratory,
University of Allahabad.

REFERENCES

- ¹ Coster, *Phil. Mag.*, **44**, 945, 1922.
- ² Idei, *NATURE*, **123**, 643, 1929.
- ³ Thibaud, *Phys. Z.*, **29**, 241, 1928.
- ⁴ del Rosario, *Phys. Rev.*, **41**, 136, 1932.
- ⁵ Magnusson, *Z. Phys.*, **79**, 161, 1932.
- ⁶ Prins and Takens, *Z. Phys.*, **75**, 743, 1932; *Z. Phys.*, **77**, 795, 1932.
- ⁷ Swirles, *Proc. Roy. Soc.*, **116**, 491, 1927; Hulme, *Proc. Roy. Soc.*, **130**, 1933; Taylor and Mott, *Proc. Roy. Soc.*, **138**, 1933; and **142**, 1933.

58. THE UPPER ATMOSPHERE

(*Proc. Nat. Inst. Sci. Ind.*, **1**, 217, 1935)

THE upper atmosphere is the name given to the part of our atmosphere which lies above the stratosphere, *i.e.*, above a height of about 20 km. or so in round numbers. Direct investigations of this region are difficult on account of its inaccessibility, but a number of indirect methods is available which are capable of throwing light on the subject. These methods can be grouped under the following headings:—

1. Direct exploration of the upper atmosphere, by means of pilot balloons, stratosphere ascents, etc. Such studies are being carried out in many meteorological stations, and the stratosphere flights have been carried out by Profs. Piccard and Cosyns in Belgium, by the National Geographical Society in the U.S.A., and by a Scientific Commission of the U.S.S.R.
2. Studies of the spectra of the aurora and the night sky.
3. Investigations of the ionisation of the upper atmosphere by radio methods, as sketched out by Dr. Mitra and other speakers.
4. Study of propagation of sound through the upper atmosphere.
5. Studies of the ozone content of the atmosphere and its variation with latitude, hour of the day and the season of the year.
6. Studies on the fall of meteors, fireballs and meteorites (Lindemann, Dobson and others).
7. Daily, seasonal and irregular changes in the earth's magnetism.

Though this discussion is properly on the 'Ionosphere', mature reflection has shown that we cannot shut out the discussion on the other topics, as they are all interrelated, and a complete picture of the upper atmosphere cannot be obtained unless the materials collected from all these sources are utilized in a synoptic study.

My own work is an attempt on these lines, and I would suggest that in future, discussions on this subject may be widened by including the other topics as well.

The particular phase of the problem which I have chosen to discuss is very ably summarised by Professor S. K. Mitra in the concluding part of his opening address which I was enabled to consult through his courtesy. I have therefore cut down much of the introduction, and proceed straight from the point where he left it.

The problem of ionisation of the upper atmosphere.

It is well known that the first suggestion that the upper air is ionised was made to account for the daily and seasonal variations—sometimes very irregular—of the earth's magnetism, probably by Balfour Stewart (1882). From the very beginning, there have been two rival views regarding the origin of the ionisation; according to the first, ionisation is caused by ejection of charged particles from the sun into the earth's atmosphere, and according to the second view, it is the ultraviolet light of the sun which causes ionisation of the molecules constituting the upper atmosphere. It is at present recognised that probably both agencies are at work, and the present-day efforts are directed more to a quantitative estimation of the relative rôles played by the two agencies.

1. *Ionisation by ultraviolet light.*

A. Schuster (1886) was probably the first to suggest that the ionisation of the upper air is due to ultraviolet radiation of the sun. This view was contested by Swann who maintained that the intensity of the solar rays is not sufficient for maintaining the requisite ionisation. He was followed by Chapman¹ and others who proceeded from the view that ionisation was due either to ultraviolet photons proceeding with the velocity of light or to corpuscles (electrons or neutral particles) proceeding with some finite velocity, both from the sun; and they tried to find out how the ionisation would vary with the time of the day (position of the sun in the sky), or with the season of the year.

In the meantime, the radio methods for the quantitative investigation of the ionised layers have been developed. These show that the ionisation is not uniform, but there are marked discontinuities at different heights where the electron-density changes rather suddenly and whence radio waves are very strongly reflected, as first postulated by Kennelly and Heaviside in 1902. So far four ionized regions (E_1 , E_2 , F_1 , F_2) have been found.

In addition to these layers, further claims have been made of a D-layer at a height of 55 kms. by S. K. Mitra and P. Syam, and of a G-layer by Kirby and Judson.²

It is now definitely settled that the ionisation of the E_1 , E_2 , and F_1 -layers is mainly due to the ionisation by the solar ultraviolet light. This was proved by the observation made in Canada by Henderson³ during the total solar

eclipse of 1932; the ionisation of the E-layer was found to diminish within the eclipse zone simultaneously with the beginning of the totality.

Further support is given by the observation that the variation of the ion-content with the time of the day for the E_1 , E_2 , F_1 layers follows closely the laws deduced by Chapman, Pedersen⁴ and others, who ascribe the ionisation to ultraviolet light from the sun. These points have been discussed in a recent paper by E. V. Appleton and Naismith.⁵ But there is great difficulty in accounting for the origin of the F_2 -layer ionisation on this basis as pointed out by the authors.

In this paper, I shall try to show that though the mathematical works of Chapman, Pedersen and others give the correct formula for the variation of the electron-content of the atmosphere with the time of the day and season, the physical assumptions regarding the cause of ionisation require revision in view of the recent laboratory work on the molecular and atomic spectra of oxygen and nitrogen. The chief constituents of the upper atmosphere are molecular O_2 and N_2 , and probably atomic O , and N ; hydrogen appears to be definitely excluded, and no helium has yet been found. Even if it exists, the argument will not be much changed. Ozone has been found to be confined between 20 kms. to 50 kms. and undoubtedly plays some important part in the phenomena observed in the lower layers.

Two assumptions form the basis of Chapman's calculations.

(a) That the sun radiates like a black body at a temperature of $6000^\circ K$, even for the ultraviolet region.

(b) That the solar radiation below λ 1350 (energy 9 e-volts) is capable of producing ionisation of some constituents of the upper atmosphere. This assumption has been subsequently modified. In his latest paper Chapman¹ tries to prove that ionisation is mostly due to atomic oxygen (I.P. 13.56 e-volts), and molecular oxygen (I.P. 16.1 e-volts), and that the temperature of the upper air which he takes to be 300° to $400^\circ K$, plays some part in promoting ionisation.

The original argument of Chapman was as follows:—

The total intensity of radiation from the sun, having a wavelength $< \lambda 1350$, is 1.61×10^{-5} times the total solar energy. So the total intensity of ionising radiation received from the sun is

$$\frac{1.61 \times 10^{-5} \times 1.93 \times 4.16 \times 10^7}{60} = 22 \text{ ergs./per sec.} \dots (1)$$

The energy required for producing a pair of ions is given by

$$\frac{9}{300} \times 4.77 \times 10^{-10} = 1.4 \times 10^{-11} \text{ ergs.} \dots (2)$$

So the solar rays can produce

$$\frac{22}{1.4 \times 10^{-11}} = 1.6 \times 10^{12} \text{ ion pairs/sec.} \dots (3)$$

when they are normally incident on the atmosphere. Let us see whether this number is sufficient to maintain the observed ionisation of the earth's atmosphere. The equation of ion-equilibrium is given by

$$\frac{dn}{dt} = I - \alpha n^2, \dots \dots (4)$$

where I is the rate of production, α is the coefficient of recombination, and n is the number of ions per cubic cm.

Now we have to find out I and α . At night we have $I=0$ and we have

$$n = n_0 / (1 + \alpha n_0 t). \dots \dots (5)$$

The value of n , n_0 can be obtained by radio methods by studying the variation of the electron-density of a layer with the progress of the night hours.

Chapman calculates from these data that $\alpha = 10^{-9}$. Again, when at midday, the stationary conditions are reached, $I = \alpha n^2$ hence if $n = 10^8$ per c.c. $I = 10^3$. If we take the depth of the atmosphere to be 300 kms. $= 3 \times 10^7$ cms., the total number of ions to be produced per second is $3 \times 10^7 \times 10^3 = 3 \times 10^{10}$. This is much less than 1.6×10^{12} , the number which the solar rays are capable of producing.

The objection against this theory is that no constituent of the atmosphere has such a low ionisation potential as 9 volts. In Table (1), the reaction potentials of all the constituents are given.

It is seen that O_2 has the lowest I.P., viz. 12.1 volts. The intensity of sunlight consisting of quanta whose energy content is larger than 12.1 e-volts is 1.5×10^{-7} times the total energy. But the whole of it is not equally effective in producing ionisation, while in Table 1 the spectrum has been assumed to extend from λ 1019 to $\lambda = 0$. We shall not be far wrong if we suppose that only one-third of the amount, i.e. $\frac{1}{3} \times 10^{-7}$ is effective. Then the energy of ionising radiation falling on one sq. cm. of the earth's surface $= 11$ ergs./sec. Hence repeating Chapman's calculations, we find that the number of ions which can be produced is 6×10^{10} . If we take into consideration the obliquity of the rays and other factors, this has to be still further reduced. This number is less than the figure 3×10^{10} , which is required according to Chapman's calculation to maintain the ionisation of the upper atmosphere.³

There is no direct evidence so far that O_2 is ionised by the solar rays to O_2^+ , because up to this time no lines due to O_2^+ (negative bands of O_2^+) have been discovered in the night sky spectrum, though this evidence alone is not conclusive against the presence of O_2^+ ions (vide infra). But the N_2^+ bands (first negative bands of nitrogen) have been found to occur in the night sky spectrum. These bands (the o-o band is λ 3910) are very prominent in the polar light, they are rather feeble in the night sky. As the excitation potential and the electron structure of the state giving rise to these bands are very accurately known

TABLE 1

Phenomenon	Active Wave-length in Å.U.	<i>e</i> -Volts	Number of quanta per cm. ² of earth per sec.	Photochemical Action.
Absorption by Ozone	2970 2300	4.136 5.40	7.2×10^{16}	Each quantum absorbed converts two O ₃ -molecules into three O ₂ -molecules.
Absorption by Oxygen	2040 1200	6.01 10.28	4×10^{14}	Each quantum absorbed produces two O ₃ -molecules.
Photo-ionisation of Oxygen (1).	1019	12.11	2.7×10^{10}	Each quantum absorbed produces O ₂ ⁺ and one electron.
Photo-ionisation of Oxygen (2)	747.8	16.5	4.2×10^6	Each quantum absorbed produces O ₂ ⁺ -excited and an electron.
Photo-ionisation of Nitrogen (1)	795.1	15.52	2.7×10^7	Each quantum absorbed produces N ₂ ⁺ -normal and one electron.
Photo-ionisation of Nitrogen (2)	660.9	18.67	10^5	Each quantum absorbed produces N ₂ ⁺ -excited and one electron.
Absorption by Oxygen	1750	7.10	7×10^{18}	Dissociation into O ³ P and O ¹ D ₂ .
Absorption by Oxygen	1324	9.32	1.65×10^{12}	Dissociation into O ³ P and O ¹ S ₀ .

they are very helpful in throwing light on the mechanism of ionisation of the upper atmosphere.

As the chart (page 223) shows, the first negative band of N₂⁺ is due to transition of the electron from a state (N ⁴S+N⁺ ³P) to the fundamental state (N ²D+N⁺ ³P).

Herzberg⁸ established that the normal state of N₂⁺ is made up of an excited N-atom (N 2p³ ²D) and a normal N⁺-ion (N⁺ 2p² ³P), and the excited state is made up of a normal N-atom (N 2p³ ⁴S) and a normal N⁺-ion (N⁺ 2p² ³P). The I.P. of N₂⁺ is 15.52 volts, and the excitation potential of N₂⁺ bands (first negative band) is 18.67 volts. It can be shown (vide Table I) that the intensity of ionising radiation energy > 15.52 *e*-volts is 5.24×10^{-10} , and for 18.67 volts, it is $< 1.5 \times 10^{-12}$, of the total solar energy. It is therefore clear, even without any calculation, that if the sun be supposed to radiate like a black body at a temperature of 6000°K, it is incapable of ionising N₂ and further exciting it to the state in which it gives N₂⁺-bands, in sufficient intensity.

Yet there is unmistakable evidence that N₂⁺ bands as observed in the night sky are due to excitation by the sun's rays, and not to electron bombardment (which is possibly the case in auroral light). For though the intensity of N₂⁺-bands in the night sky is rather feeble compared to that in the auroral light, Slipher⁷ has shown, at the Lowell

Observatory, Arizona, that the negative bands are obtained very strongly from the evening sky, when the last rays of the sun are disappearing from the upper atmosphere, or from the morning sky, when the first rays are illuminating the upper atmosphere. His exact remarks are:—

'But the negative nitrogen bands typical of auroral display spectra do not accompany this chief yellow line (green) in the sky, except when auroral displays are actually present. However, these nitrogen bands, I found, could be photographed in the morning and evening skies if brief exposure were made at the moments, when the last and first traces of sunlight touch the high atmosphere. Thus the day, as it were, begins and ends with a sort of auroral flash.'

Slipher's statement that the N₂⁺ bands do not at all occur in the quiet night sky, which is absolutely free from all auroral displays, is not quite correct. Sommer⁸ found these bands in 2 out of 30 plates of quiet night sky spectrum taken at Göttingen, and subsequently they have been found by Vegard, Du Fay,⁹ Cabannes, and Gauzit.¹⁰

The important point to infer from Slipher's observation is that the sunlight produces N₂⁺ in the excited state directly and in course of the night, the de-excitation by emission of the lines of negative band continues.

We may further explain why the N₂ molecule is directly

excited to N_2^+ . The normal N_2 molecule is composed of ($N^4S + N^4S$), when it is photo-ionised, the light electron of one N-atom passes to infinity leaving N^+ in the normal 3P -state. So the new ion is made up of ($N^4S + N^+^3P$). But as fig. 2 (p. 223) shows, this is the excited state of normal N_2^+ ion, which is made up of ($N^2D + N^+^3P$). This curious fact was, as mentioned already, discovered by Herzberg.

We are therefore within the horns of a dilemma. All experimental evidence shows that the sun sends out rays which are capable of ionising the constituent molecules of the upper atmosphere, at least N_2 . At the same time we find that the sun, if regarded as a black body at a temperature of $6000^\circ K$., is incapable of emitting in sufficient intensity radiation of such short wavelength as will maintain the ionisation.

In order to solve this difficulty I wish to postulate, though with a certain amount of hesitation, that the sun emits in sufficient intensity the lines of the Lyman series of hydrogen as well as the fundamental resonance lines $1s^2$, $1S_0 - 1s\ 2p\ ^1P_1$ of Helium, $\lambda\ 584$, and possibly the fundamental lines of a few more elements. In other words, if it were possible for us to take a spectrum of the sun below $2900\text{\AA}$ units, the Lyman series as well as the principal lines of He and other elements like Fe would appear as intensely bright emission lines on a much feebler continuous background.

2. The ultraviolet spectrum of the sun.

Let us now see how far this postulate can be justified. The sun as well as the stars are generally assumed to radiate like a black body, but there appears to be no justification either experimental or theoretical for such an assumption. The spectra of all heavenly bodies is cut off, owing to absorption by atmospheric ozone at *ca.* $\lambda\ 2900\text{\AA}$ U., and measurements are usually confined to wavelengths between $\lambda\ 3000\text{\AA}$ U. and $\lambda\ 5000\text{\AA}$ U. Even when corrected for Fraunhofer absorption and general scattering, the curve is found to deviate strongly from what we should expect if the emission followed the black body law (vide Böttlinger, *Handbuch d. Astrophysik*, 5/1, or discussion given in *Treatise on Heat*, by Saha and Srivastava, p. 619, 2nd edition) even for this limited region. As a matter of fact, if we consider the physical composition of a star, it appears rather improbable that emission from it would be of the nature of a black body, and the radiation is likely to be more of the type which we obtain for heated metals.

A star consists of a central core, usually called the photosphere, made up of highly condensed matter, which is enveloped by a thinner atmosphere containing atoms, molecules, and ions, the temperature in this atmosphere gradually falling outwards. Fraunhofer lines are produced as continuous light is absorbed by atoms, ions, and molecules in its passage through the outer atmosphere. It is found

that these lines are not absolutely black, but there is always some residual intensity in the lines. For example, if we take the H_α -line due to absorption by the H-atom, the residual intensity was found to be .25 of the intensity of the continuous spectrum. The present author pointed out long ago (see Mitchell, *Eclipses of the Sun*, 1st edition, 1923, p. 311) that the residual intensity is due to emission by the atoms or ions present in the atmosphere. The intensity would be nil only, if the temperature of the absorbing layers was very low.

In Wolf-Rayet stars, and nebulae, we obtain bright lines, due to commoner elements like H, He, N, He^+ , N^+ ... superposed on a much feebler continuous background.

It appears therefore that the nature of emission from a star is a very complex phenomenon. A pioneering step for solving this problem was taken by Rosseland,¹¹ who showed that in considering the emission from a stellar atmosphere we must consider the possibility of ultraviolet light from the interior exciting the atoms to fluorescence. He showed in particular that if an L_β -quantum ($\nu/R = \frac{1}{1^2} - \frac{1}{3^2}$) coming from the photosphere is absorbed by an H-atom in the atmosphere, the excited H_3 -atom may revert back to the normal stage, (1) either by the direct transition ($3 \rightarrow 1$), or (2) in two stages, viz. ($3 \rightarrow 2$) and ($2 \rightarrow 1$), but the probability of the latter process is greater than that of the former. Thus the L_β -quantum will be split up, at the upper atmosphere, into an L_α ($2 \rightarrow 1$) and an H_α ($3 \rightarrow 2$) quantum. Further, most of the ultraviolet lying beyond the Lyman limit will ionise the H-atom as they come out. But in the outer atmosphere, the free electrons will combine with the H-nucleus in different orbits, and the excited atoms so produced will, instead of emitting the corresponding Lyman quantum, emit quantum of Balmer or Paschen or a higher series plus an L_α -quantum. Thus, by this process ultraviolet light coming from the photosphere is dammed by H-atoms and converted into line radiation, and the net effect is that the resultant spectrum will show extraordinary strength for the first lines of the series, viz. for L_α and H_α . These considerations were utilised by Zanstra¹² for explaining nebular luminosity, and on such considerations he was able to construct a successful theory of nebular emission which has been further extended by Beals¹³ to emission from Wolf-Rayet stars.

The ideas have been further applied by Woolley¹⁴ to account for the observed central intensity of Balmer lines in the solar spectrum. He obtains in fact the result that the residual intensity of the H_α -line would amount to .40 of the intensity of the continuous spectrum. This is much larger than the figure of .25 which was deduced by Minnaert¹⁵ on the basis of his spectrophotometric measurements. Woolley did not calculate the residual intensity of the L_α or L_β -lines. This is being attempted by the present writer, but the results which have been obtained can be regarded

only as provisional. It is found that the intensity of the α -radiation is much stronger than that of the continuous spectrum of a black body at a temperature of 6000°K. As these calculations are very tedious, they will be published elsewhere, but a shorter, though not satisfactory, method of arriving at the result is indicated below.

It has been shown by Minnaert¹⁵ that the H_α -absorption in the sun dams an amount of solar energy which is equivalent to a strip of the continuous spectrum, about 4.17 Å units in breadth. We can therefore calculate the total number of H_α -quanta held back by absorption due to H_2 -atoms. This is given by (see note 2)

$$N_v = 8\pi^2 R^2 c \left(\frac{kT}{ch} \right)^3 \frac{x_0^3}{e^{x_0} - 1} \frac{\Delta\lambda}{\lambda}$$

Now putting the proper figures in the above formula, we have

$$N_v = 8\pi^2 R^2 \cdot 2 \cdot 10^{18} \text{ quanta.}$$

So the number dammed by unit surface of the sun

$$\frac{N_v}{4\pi R^2} = 11 \cdot 10^{18} \text{ quanta.}$$

We take the residual intensity of H_α to be .25. Then the number of quanta due to fluorescence = $\frac{1}{4}$ number actually dammed, the number of quanta emitted by the $H(2)$ atoms per cm.² of the sun's surface is given by

$$n_v = 3 \cdot 10^{18} \text{ approximately.}$$

Let us now try to arrive at an estimate of the number of Lyman α -quantum which are expected to be emitted by the sun. This will be much larger than the number of H_α -quanta. Let us put this equal to $3x \cdot 10^{18}$, $x > 1$.

Here x can be accurately calculated, but we need not do it at the present moment. But if we take the number of Lyman α -quanta in the continuous spectrum of the sun, supposed to radiate like a black body at $T=6000^\circ\text{K}$, we obtain when we assume that $\Delta\lambda/\lambda$ for L_α is equivalent to $\Delta\lambda/\lambda$ for H_α ,

$$n_v \text{ for } L_\alpha = 10^{14} \text{ (approximately),}$$

i.e., the fluorescent emission of L_α is at least 40,000 times more intense than the continuous emission in the same region.

As remarked before, this calculation is given with a certain amount of reserve.

The other lines of the Lyman series will also be several thousand times stronger than the continuous background of sunlight.

The remarks which have been made regarding the intensity of the Lyman lines holds for all principal lines of elements lying in the ultraviolet, though calculations are more difficult in such cases as transition probabilities are not known. The only other elements which need be considered are He, O, N, He^+ and Fe and Fe^+ . As regards He, it is well known that no lines are found in the Fraunhofer spectrum, though such lines are very strong in chromospheric emission, and He^+ 4686 is found as a strong line in the middle chromosphere. Recently H. D. and H. W. Babcock¹⁶ found that the line $\lambda 10830.3$ ($2^3\text{S}-2^3\text{P}$) and the

He^+ -line $\lambda 10123.83$, $\nu = 4R \left[\frac{1}{2^2} - \frac{1}{(2+\frac{1}{2})^2} \right]$ as diffuse absorption lines on the solar disc. This discovery indicates that the HeI-resonance line ($1^1\text{S}_0 - 2^1\text{P}_1 = \lambda 584$) as well as the He^+ -line $4R \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$, $\lambda 304$, would be emitted in very great intensity from the solar disc.

3. Passage of ultraviolet light through the earth's atmosphere.

If the above speculations be correct, we should get the following monochromatic rays emitted in great intensity from the sun.

It now remains to show that some of these rays cannot only maintain the necessary ionisation, but can also account for the special features of the night sky spectrum. In appendix I, we give a detailed summary of the night sky spectrum. We first discuss the ionisation of N_2 and the occurrence of band lines of N_2^+ in the night sky.

The N_2 -ionisation.

The N_2 -ionisation is established on sure grounds from the occurrence of the first negative bands of nitrogen. Observations by Dufay and Gauzit¹⁰ show that in the night sky we obtain lines corresponding to $\nu'=8$. The energy of the quantum can be easily calculated. This is nearly 21.10 e-volts (*vide infra*).

Thus the energy of the quantum of He-resonance radiation $\lambda 584$, which is equivalent to 21.20 volts, is quite sufficient to knock out an electron from N_2 , and leave it

TABLE 2

Line	1215	1026	987	584	537	304	1641
Origin	L_α (H)	L_β (H)	L_γ (H)	$I_5^2 \text{ } ^1\text{S}_0 - ^1\text{P}$ He	He	He^+ $4R \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$	He^+ $4R \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$
Energy in e-volts	10.15	12.03	12.68	21.12	22.98	40.58	7.52

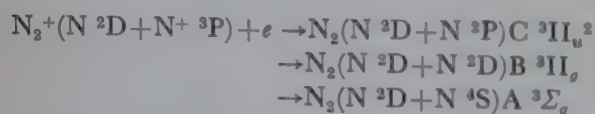
in a state when it can emit the negative bands. As pointed out before, N_2 consists of $N(^4S) + N(^4S)$. When an electron is knocked off, we get the molecule $N(^4S) + N^+(^3P)$. But as Herzberg proved, this is the excited state of N_2^+ and the normal state is obtained when the electron passes from $^4S \rightarrow ^2D$, i.e. to a state $\overline{N}^2D + N^+^3P$. Such a transition seems to be paradoxical but, nevertheless, we have to admit it. A consideration of the Franck-Condon diagram for N_2 and N_2^+ shows that $\nu' = 0$ to 8 may be directly excited, as r_0 for the normal N_2 is 1.094×10^{-8} , while r_0 for the upper electronic states of N_2^+ is $1.071 \cdot 10^{-8}$ cm.

The night sky spectrum.

As described in the appendix, the night sky spectrum shows, beside the first negative bands, the following bands due to:—

- The Second Positive Group .. $B^3\Pi_u(^2D+^2D) \leftarrow C^3\Pi_u(^2D+^3P)$
 The First Positive Group .. $A^2\Sigma_g(^2D+^4S) \leftarrow B^3\Pi_u(^2D+^2D)$
 Vegard-Kaplan bands .. $X(^4S+^4S) \leftarrow A^3\Sigma_g(^2D+^4S)$

It appears that the occurrence of all these bands can be explained if we suppose that the normal N_2^+ -molecule ion, which has got the electron structure $(N^2D + N^+^3P)$, receives an electron and gets neutralized in different excited states as follows:—



It will be seen that one atom in all the initial levels of N_2 excited is in N^2D -state. This is because the normal state of N_2^+ has its N-atom in the N^2D -state. The N^+ -atom in N_2^+ is in the state $N^+2p^2^3P$ and when it receives the electron in the $2p$ -shell, the $2p^3$ -configuration gives rise to $^4S, ^2D, ^2P$ which, combined with the N in the N^2D -state, gives rise to the levels from which the observed bands are obtained by subsequent electron transition.

Thus the occurrence of the bands in the night sky is merely a consequence of recombination of N_2^+ produced by sunlight with free electrons during the night, and all its details are explained by the peculiar spectral properties of the N-atom and the N_2^+ -molecule. The emission of N_2^+ -band is due to de-excitation of N_2^+ excited, which is produced by sunlight to normal N_2^+ . As the recombination is going on throughout the night, we observe the bands throughout the night.

4. Atomic nitrogen in the night sky spectrum.

The occurrence of atomic nitrogen in the night sky spectrum is rendered probable by the existence of a line λ 5208, in the photographs obtained by Slipher. This has

been ascribed by Sommer¹⁷ to the forbidden transition of nitrogen $N(^4S \rightarrow ^2D)$. The identification is not quite on sure grounds on account of the close proximity of the line with the N_2 -band, 5228.3 (3,0).

Atomic nitrogen may arise by predissociation of the excited N_2 -levels which are responsible for the emission of the nitrogen band lines. For, according to the present hypothesis, the excited levels are due to the capture of the electron by N_2^+ in the $2p$ -level. The nuclear distance for N_2 and for each of the excited levels of N_2 are as follows:—

TABLE 3

Level	X $^1\Sigma$	A $^3\Sigma$	B $^3\Pi$	C $^3\Pi$	$N_2^+X^3\Sigma$	$N_2^+B^3\Sigma$
r_0	1.094	1.291	1.201	1.14	1.113	1.071

We may suppose, following the Franck-Condon principle, that the capture of an electron does not immediately change the nuclear distance. Hence, after recapture, the N_2 molecule will be in the vibrational state in which the nuclear distance is likely to remain unchanged. As the r_0 -values for B and A levels are very different from r_0 for N_2^+ , it is likely that the state of the neutral molecule will be in a highly excited vibrational state and it is probable that a large proportion of B and A level N_2 -molecules will predissociate, the first into N^2D and N^2D , the second into N^4S and N^2D , but exact calculation of the vibrational numbers of the states is not possible at the present moment. If N^2D -atoms are produced in these ways, they will revert to the 4S -state after emission of the line λ 5207.

5. The oxygen and the ozone problem.

We are on less sure grounds when we consider the oxygen problem; as our knowledge of the molecular spectrum of neither O_2 nor O_2^+ is so satisfactory as that of N_2 ; in fact it may be considered extremely meagre.

One of the most curious facts of observation is that no lines due to O_2 or O_2^+ has yet been discovered with certainty either in the night sky or the aurora. Atomic oxygen is represented by the famous green line λ 5577.350, $2p^4(^1D \rightarrow ^1S_0)$, and possibly also by the lines λ 6300,* λ 6363, $2p^4(^3P_{12} \rightarrow ^1D_2)$, though these last are blended with certain lines which Sommer ascribes to O_2 atmospheric bands. They may as well belong to N_2 first positive bands.

The absence of O_2 and O_2^+ lines do not indicate that the molecular O_2 is absent. As shown in the chart, all the known bands of O_2 and O_2^+ are in the ultraviolet with the single exception of the atmospheric bands. The most important are the Runge-Schumann bands starting from λ 2000 and passing to continuous absorption at λ 1751. The absorption continues up to λ 1210 Å.U.

*Note added during correction: Cabannes, *Comptes Rendus*, Vol. 200 (1935), announces that he has unmistakably obtained the red lines.

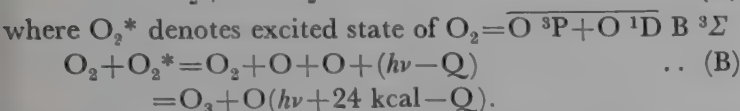
It has been shown by Herzberg that these bands denote transition from $O_2(^3P+^3P)^3\Sigma \rightarrow O_2(^3P\ ^1D_2B)\ ^3\Sigma_u$ and the continuous absorption at $\lambda\ 1751\ \text{\AA}$. U. correspond to the dissociation of O_2 into $O\ ^3P$ and $O\ ^1D_2$ we have



This absorption is quite heavy, and extends up to $\lambda\ 1300$. According to Lyman, O_2 is transparent to wavelengths between $\lambda\ 1100$ and $\lambda\ 1217.7$. In fact 3 cm. of oxygen at N.T.P. is found to transmit both $\lambda\ 1100$ and $\lambda\ 1205$.

Formation of ozone.

It is supposed that the Runge-Schumann absorption converts O_2 into ozone according to the process indicated below:—



(B) indicates that O_2^* or excited oxygen collides with O_2 , and dissociates it into two atoms, and simultaneously one of these O-atoms reacts with O_2 to form O_3 . According to calorimetric relation



The reaction is exothermic, and takes place easily.

The energy set free is $h\nu + 24\ \text{kcal} - Q$, and if a wavelength of $\lambda\ 2040$ is used, $h\nu = 141\ \text{kcal}$. We have therefore the energy set free $141 + 24 - 117 = 48\ \text{kcal}$, and this is quite sufficient to raise the remaining O-atom to the $O\ ^1D_2$ -state, as shown below:—



This $O\ ^1D_2$ -atom reacts more readily with another O_2 -atom and forms another O_3 -molecule, and 72 kcal of heat produced. Thus, as Warburg experimentally established long ago, one quantum of light of wavelength $< \lambda\ 2040$ produces two molecules of O_3 .

Let us suppose that all quanta between $\lambda\ 2040$ and $\lambda\ 1250$ are effective in producing ozone. If the sun be assumed to behave like a black body, the number of such quanta entering the earth's surface normally is given by (*vide note 2*).

$$3 \cdot 10^{17} \cdot [I_1(x_1) - I_1(x_2)],$$

where

$$I_1 = \int_x^\infty \frac{x^2}{e^x - 1} dx.$$

Now $x_1 = 11.6$, $x_2 = 19.3$, corresponding to $\lambda\ 2040$ and $\lambda\ 1200$, $I_1(x_1) = 1.46 \times 10^{-3}$, $I_2 \simeq 10^{-6}$ and we have $n_v \simeq 4.4 \cdot 10^{14}$ quanta so the number of ozone molecules formed $= 10^{15}$ per second by normally incident sunlight.

De-ozonisation.

Again it is found that all radiation from $\lambda\ 2900$ up to $\lambda\ 2300$ are absorbed by O_3 molecules, which are thereby

converted to O_2 . It can be easily shown that the number of such quanta entering the earth's atmosphere normally $= 7.10^{15}$ and each quantum decomposes two O_3 -molecules, forming $3O_2$ -molecule. So the number of O_3 -molecules which disappear $= 14 \cdot 10^{15}$.

We thus find that ozone disappears 14 times as fast as it is formed. If this were the case, there would be no equilibrium. But we must have

$$\frac{d[O_3]}{dt} = 2n_2 - 2n_3, \quad \frac{d[O_2]}{dt} = 2n_3 - 2n_2,$$

where $[O_3]$ denotes the concentration of ozone molecules, and n_3 the number of quanta absorbed by ozone, $n_2 =$ number of quanta absorbed by oxygen, other factors like collision being neglected, and if we have equilibrium, we must have $n_3 = n_2$. This shows that between $\lambda\ 2040$ and $\lambda\ 1200$, the number of quanta in the sunlight must be as numerous as the number between $\lambda\ 2900 - \lambda\ 2300$. Hence the sun cannot behave like a black body between $\lambda\ 2040$ and $\lambda\ 1200$. There must be strong emission lines in this region. In fact we have such lines in

$$He^+ \lambda\ 1640, \nu/4R = \frac{1}{2^2} - \frac{1}{3^2},$$

and probably also in L_α due to H-atom. We utilise the observation of Hopfield, that about 10 cm. of oxygen at N.T.P. is needed to completely absorb $\lambda\ 1215$.

Supposing that O_3 formation is due to $\lambda\ 1215$ and $\lambda\ 1641$, we can calculate the depth at which ozone formation begins. This is the height above which the superincumbent number of oxygen molecules equals the number of molecules contained in about 10 c.c. of oxygen at N.T.P. Calculation shows that this height is about 20 km. So this is the height at which L_α is completely absorbed, and ozone formation ends. This is in accordance with the observations of Götz and Meetham¹⁸ and Regener.¹⁹

Occurrence of oxygen.

Oxygen is represented by:

1. The green line due to the forbidden transition $p^4\ ^1D_2 - ^1S_0$.
2. The red lines due to the forbidden transition $p^4\ ^3P_{12} - ^1D_2$.
3. Some bands in the red which are provisionally identified by Sommer with some telluric lines.

It is thus remarkable that oxygen is represented only by atomic lines, and no lines due to the molecule are identified with certainty. Let us see what may be the cause of this remarkable difference between the occurrence of N_2 and O_2 .

For this purpose, we give an energy-level diagram of the known bands of O_2 , and O_3^+ . We at once perceive that as regards oxygen, we are in a rather very disadvantageous position, because all the stronger bands of O_2 and O_3^+ are in the ultraviolet and infra red regions where observations are either impossible or difficult. Hence the absence of

O₂-band lines in the night sky and the auroral spectrum is no proof that the upper atmosphere contains no molecular oxygen.

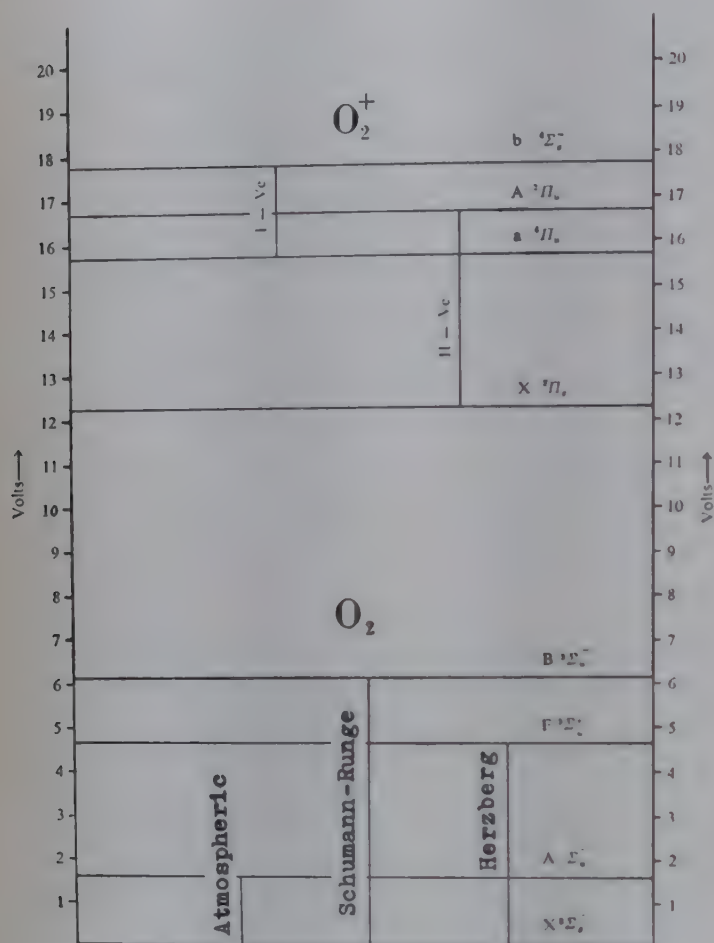


Fig. 1

In fact, as Table 2 shows, of all atmospheric components, O₂ has the lowest I.P., viz. 12.11 e-volts, and about 10¹⁰ electrons and O₂⁺-ions can be produced by sunlight by the ionisation of O₂ alone. Though this number is not sufficient to maintain the ionisation observed, it is clear that if the hypothesis of strong emission of L_β, L_γ-lines can be established on sure grounds, the observed ionisation can be traced to this source. This ionisation must correspond to that of the E-layer.

But the molecular energy diagram makes it almost certain that the O₂⁺-ion produced in this way is made up of O³P + O⁴S. When, during the night, this O₂⁺-ion combines with a free electron, normal O₂ will be produced preferably.

But a second ionisation potential of O₂ has been discovered at 16.5 e-volts. The electron-structure of the atoms composing the O₂⁺-molecule-ion produced at this potential is not yet known, but some conjectures may be advanced.

Let us consider the following energy-relationships:—

$$\begin{aligned} \text{O}_2 &= \text{O}^+(^4\text{S}) + \text{O}^3\text{P} + e - 18.65 \text{ e-volts} \\ 18.65 &= \text{I.P. of O} + D_0 = 13.56 + 5.09. \end{aligned}$$

$$\begin{aligned} \text{O}_2 &= \text{O}^+(^2\text{D}) + \text{O}^3\text{P} + e - 21.95 \text{ e-volts} \\ 20.61 &= 18.65 + 3.30 (= \text{O}^+2\text{D} - \text{O}^+4\text{S}). \end{aligned}$$

$$\begin{aligned} \text{O}_2 &= \text{O}^+(^2\text{P}) + \text{O}^3\text{P} + e = 23.64 \text{ e-volts} \\ 23.64 &= 21.95 + 1.69 (= \text{O}^2\text{P} - \text{O}^2\text{D}). \end{aligned}$$

$$\text{O}_2 = \text{O}^1\text{D}_2 + \text{O}^+(^4\text{S}) - 20.61 \text{ e-volts.}$$

$$\text{O}_2 = \text{O}^1\text{D}_2 + \text{O}^+(^2\text{D}) - 23.91 \text{ ,,}$$

$$\text{O}_2 = \text{O}^1\text{S}_0 + \text{O}^+(^2\text{D}) - 26.11 \text{ ,,}$$

$$\text{O}_2 = \text{O}^1\text{S}_0 + \text{O}^+(^2\text{P}) - 27.80.$$

In all these calculations, we use O¹D₂—O³P = 1.96 e-volts, O¹D₂—O¹S₀ = 2.21 e-volts.

Of the phenomena indicated by the above figures, only the decomposition of O₂ to O⁺ ⁴S and O⁺ ³P has been observed by Stueckelberg by the method of cathode ray bombardment.

Now the energy required to produce the state of the O₂⁺-ion composed of the atom in the states described above can be obtained if we subtract from the energy-values given above the value of Q, the energy required to dissociate the molecule-ion. Thus the first observed I.P. of 12.11 e-volts, according to Mulliken (*Phys. Rev.* 44), is due to the formation of the molecule-ion (O⁺ ⁴S + O³P)²II. The heat of dissociation is 18.65—12.11 = 6.54 e-volts. It may be that the O₂⁺-ion produced at 16.5 e-volts is composed of (O⁺ ²D + O³P). All these energy-states have to be established by subsequent investigations.

It is clear that if there are strong violet emission lines in the solar ultraviolet spectrum of sufficient energy, O₂ may be ionised by their action to the O₂⁺-state as envisaged above. These O₂⁺-ions may, in the course of the night, capture an electron, and may be converted to different molecular states of O₂. These may *predissociate*, forming O¹D₂ or O¹S₀-atoms. The green and red auroral radiation may be due to emission by the excited atoms produced in this way. There appears to be no other way of getting the green line throughout the night except as an after-effect of recombination of O₂⁺ (excited) with the electron. But the hypothesis leaves it unexplained why the green line is so much more intense than the other lines. For this we shall have to wait till our knowledge of the spectrum of O₂ improves.

APPENDIX I.

THE NIGHT SKY AND THE AURORAL SPECTRUM

In the foregoing pages, we have so often talked of the night sky and the auroral spectra that it is probably necessary to give some idea of the conclusions which we can deduce from their study regarding the physical state of the upper atmosphere. Both spectra are due to excitation

The chief constituents of the atmosphere are O_2 , N_2 , O_3 , H_2O , CO_2 , Λ , and minute quantities of other gases. Of these CO_2 can be neglected as far as the upper atmosphere is concerned. Hydrogen and helium, which were at one time postulated to occur in comparatively greater abundance in the upper atmosphere, may also be considered as non-existent, as neither in the night sky spectrum, nor in the aurora, nor in any meteoric flash has any line due to these elements been identified.

Nitrogen is represented by the following system of bands:

- Deslandres' diagrams of these bands are added for the sake of further elucidation. An energy-level diagram of N_2 is also added, as otherwise, it is difficult to have a complete picture of the mechanism of excitation.

$$v = 25566.0 + (2396.22v' - 24.07v'^2 - 636v'^3) - (2191.02v'' - 16.196v''^2)$$

where $\nu_0=25566.0$ cm. is equivalent to 3.156 volts. The energy of excitation of the (0,0)-band is 18.68 volts. The



First Negative Bands of N₂ (due N₂⁺).

$v' \backslash v''$	0	1	2	3	4	5	6	7	8	9	10	11
0	<u>3914·4</u>	<u>4278·1</u>	<u>4709·3</u>	<u>5228·3</u>	<u>5864·7</u>							
1	<u>3582·1</u>	<u>3884·3</u>	<u>4236·5</u>	<u>4651·9</u>	<u>5148·8</u>	<u>5754·4</u>						
2	<u>3308·9</u>	<u>3563·9</u>	<u>3857·9</u>	<u>4199·2</u>	<u>4599·9</u>	<u>5076·5</u>	<u>5653·2</u>					
3	<u>3078·2</u>	<u>3298·7</u>	<u>3548·9</u>	<u>3835·4</u>	<u>4166·8</u> } <u>4166·4</u> }	<u>4554·4</u> } <u>4553·2</u> }	<u>5012·4</u> } <u>5010·8</u> }	<u>5563·8</u> } <u>5560·8</u> }				
4		<u>3076·4</u>	<u>3293·4</u>	<u>3558·3</u>	<u>3818·1</u>	<u>4140·7</u>	<u>4515·9</u>	<u>4958·0</u>	<u>5485·8</u>			
5					<u>3532·6</u>		<u>4121·3</u> } <u>4120·7</u> }	<u>4485·9</u> } <u>4485·3</u> }	<u>4913·2</u>	<u>5420·8</u>		
6								<u>4110·9</u>	<u>4466·6</u>	<u>4881·7</u>	<u>5372·3</u>	
7										<u>4459·3</u>	<u>4864·4</u>	<u>5340·2</u>
8											<u>4466·6</u>	<u>4864·4</u>
9												<u>4489</u>
10							<u>2987·5</u>	<u>3174·4</u>	<u>3381·5</u>	<u>3612·6</u>		
11								<u>3033·0</u>	<u>3222·7</u>			

vibrational state $v'=8$, which appears to be the highest obtained in the night sky spectrum, requires 21.10 volts. These lines require the highest excitation for their production.

The lines obtained in the night sky are underlined. The ultraviolet lines were obtained by Dufay and Gauzit.

Difference of behaviour in the night sky and the aurora.

These bands are very intense in the aurora, but are rather faint in the night sky. In fact, in the former, 3914 (0,0), 4278 (1,0) sometimes exceed even the green line in intensity. But in the latter, they are very feeble, and $\lambda 4278$ is not sometimes observed even after long exposure. The bands $\Delta n=0$ are the strongest.

The second positive group is due to the transition ($^3D^3P$) $C^3II-(^2D^2D) B^3II$ and is represented by the formula

$$\nu = 29670.6 + (2020.0v' - 26.40v'^2 + 1.158v'^3) - (1719.64v'' - 14.47v''^2).$$

These lines were first found by Sommer in the night sky and by Vegard in the aurora. These bands are very bright in the night sky, but faint in the aurora. The line 3555 (8,9) is found to be very intense in the night sky; the reason being unknown. (Table 5).

The lines obtained in the night sky are underlined. The lines (12, 8), (13, 9) are the bands which are observed to predissociate in the laboratory, giving rise to two

2D -atoms. These bands are not observed owing to ozone absorption. But presumably owing to predissociation a considerable proportion of N 2D -atoms will be produced in the daytime in this way.

The first positive group is due to the transition ($^2D^3D$) $B^3II-(^2D^4S) A^3\Sigma$ and is represented by the formula

$$\nu = 9518.6 + (1718.40v' - 14.437v'^2) - (1446.46v'' - 13.929v''^2).$$

The bands observed in the night sky are underlined. They were observed by Vegard (*Norw. Geophys. Pub.* 9, No. 4, 1932) in the aurora, in which they are much fainter than the second positive group, but in the night sky they are very intense.

The Vegard-Kaplan bands are due to the intercombination between singlet and triplet systems and to the transition ($^4S, ^3D$) $A^3\Sigma-(^4S, ^4S) X^1\Sigma$. They are represented by the formula:—

$$\nu = 49774.4 + (1446.46v' - 13.93v'^2) - (2345.16v'' - 14.445v''^2).$$

After emission of these bands, the N_2 -molecule reverts to the normal state. We get only one part of the Vegard-Kaplan bands in the night sky, as the other part is in the far ultraviolet.

It is only recently that the Vegard-Kaplan bands have been discovered in the night sky (see Cabannes and Dufay,

TABLE 5

The Second Positive Group of Nitrogen.

$n' \backslash n''$	0	1	2	3	4	5	6	7	8	9
0	<u>3371</u>	<u>3577</u>	<u>3805</u>	<u>4059</u>	<u>4344</u>	<u>4666</u>				
1	<u>3159</u>	<u>3339</u>	<u>3536</u>	<u>3755</u>	<u>3998</u>	<u>4269</u>	<u>4574</u>	4917		
2	2977	<u>3136</u>	<u>3309</u>	3500	<u>3710</u>	<u>3942</u>	<u>4201</u>	4490	4814	
3	2820	2962	<u>3116</u>	<u>3285</u>	<u>3469</u>	<u>3671</u>	<u>3894</u>	<u>4141</u>	4416	4723
4		2814	2953	<u>3104</u>	<u>3267</u>	<u>3446</u>	<u>3642</u>	3857	<u>4094</u>	4356
5					<u>3102</u>	3263	3437	<u>3628</u>	3837	<u>4059?</u>
6						<u>3115</u>	3274	3446	<u>3634</u>	3840
7								3309	<u>3482</u>	<u>3670(?)</u>
8								<u>3217</u>	3380	3555
9								3171		3502

TABLE 6

The First Positive Group of Nitrogen

$n' \backslash n''$	0	1	2	3	4	5	6	7	8	9
0	10491									
1	<u>8911.57</u>									
2	7753.05	<u>8722.28</u>	9927							
3		<u>7626.13</u>	8541.73	9657						
4		<u>6788</u>	<u>7504.0</u>	8369.02	9409					
5		<u>6127</u>	<u>6704</u>	<u>7386.5</u>	8204.62	9180				
6			<u>6076</u>	<u>6624</u>	<u>7273.0</u>	<u>8047.26</u>				
7				6014	<u>6545</u>	7164.6	<u>7896.28</u>			
8					5959	<u>6469</u>				
9						<u>5906</u>	<u>6394</u>			
10						5442	<u>5855</u>	<u>6323</u>		
11							5407	5804	6252	
12								5375	<u>5755</u>	<u>6185</u>
13										

Comptes Rendus, vol. 200, p. 1504; 1935). The most intense lines are (2,15), (3,15), (2,14), (4,15), i.e. $\Delta n=12,11$. In fact the bands (2,14), and (4,15) appear to be identical with λ 4435, 4220Å, which were observed by Lord Rayleigh to occur strongly in the spectrum of the night sky (*Proc. Roy. Soc.*, vol. 131, p. 376; 1931). The reason that lines having $\Delta n=10,11$ appear strongly is to be sought in the Franck-Condon principle, for r_0 for the initial $A^3\Sigma=1.291 \times 10^{-8}$ cm., for the final $X^1\Sigma=1.094 \times 10^{-8}$ cm. As these are very different, transition from $A^3\Sigma$ can take place to that vibrational state of $X^1\Sigma$ where its vibration quantum number is very large.

NOTE 2

Number of Quanta in the Solar Spectrum whose energy-value exceeds a certain limit.

Let the sun be considered as a black body at a temperature T , and having a radius R . The energy radiated

per second by the sun within the frequency interval $d\nu$ is given by:—

$$\pi R^2 \cdot c \cdot \rho_\nu \cdot d\nu, \quad \dots (1)$$

where ρ_ν =energy density of black body radiation and is given by Planck's Law

$$\rho_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/kT} - 1}. \quad \dots (2)$$

The number of quanta emitted is obtained by dividing (1) by $h\nu$. We thus obtain:

$$dN_\nu = \frac{8\pi^2}{c^2} R^2 \cdot \frac{\nu^2}{e^{h\nu/kT} - 1} \cdot d\nu. \quad \dots (3)$$

Let us now put $h\nu/kT = x$. We have then

$$dN_\nu = 8\pi^2 \cdot R^2 \cdot c \cdot \left(\frac{kT}{hc}\right)^3 \cdot \frac{x^2}{e^x - 1} \cdot dx. \quad \dots (3')$$

TABLE 7
The Vigard-Kaplan Bands

ν'	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
0				2332.8	2461.6	2608.8	2760.6	2935.7			3600 3608	3886 3889 (1)	4216 4220 (1)	4601 4603	5055 5062 (2)					
1					2377.5	2509.8	2655.5		2997	3197.5	3424 2426 (2)	3681 3685	3976 3979 (1)	4316 4317 (1)	4714 4719 (1)	5185 5185 (0)				
2						2424.2	2560.9	2710.1				3500 3501 (1)	3765 3769	4069 4073 (3)	4421 4425 (5)	4893 4898 (4)	5321 5324 (0)			
3													3590 3582 (1)	3853 3855 (3)	4167 4171 (5)	4531 4536 (3)	4957 4962 (0)			
4														3663 3669 (7)	3945 3950 (3)	4270 4270 (4)	4647 4650 (1)	5068 5083 (2)		
5																4042 4056 (2)	4378 4382 (7)	4768 4768 (1)		
6																	4144 4144 (2)	4491 4493 (1)		
7																	3937 3936 (2)	4294 4252	4610 4616 (2)	
8																			4361 4361 (1)	

If now we wish to find out the number of quanta whose energy exceed a certain limit ($h\nu_0$) we have to evaluate the integral

$$I_1 = \int_{x_0}^{\infty} \frac{x^2}{e^x - 1} dx, \quad \dots (4)$$

where $x_0 = h\nu_0/kT$.

Now $\omega = 4.65 \times 10^{-3}$ in radians, and if we take $T = 6000^\circ\text{K}$, we obtain after putting the values of k, c, h ,

$$N_\nu = 3.10^{17} \cdot I_1 \text{ (approximately)} \quad \dots (5')$$

Number of Quanta emitted within the wavelength λ_1, λ_2 .

Let $x_1 = h\nu_1/kT$, $x_2 = h\nu_2/kT$, where $\nu_1 = c/\lambda_1$, $\nu_2 = c/\lambda_2$.

We have then

$$N_{\nu_1-\nu_2} = 3.10^{17} \cdot (I_1 - I_2).$$

When $\lambda_1 - \lambda_2$ is small, it can be easily shown that $N_{\nu_1-\nu_2}$ is given approximately by:—

$$N_{\nu_1-\nu_2} = 3 \times 10^{17} \cdot \frac{x_0^3}{e^{x_0} - 1} \cdot \frac{\Delta\lambda}{\lambda_0},$$

where λ_0 is the mean wavelength, $\frac{\lambda_1 + \lambda_2}{2}$.

Tables of $\log I$, and $\log I_2/6.494$ (vide infra) have been prepared by Zanstra in connection with problems of

nebular luminosity and are given in Table 8. With the aid of these tables, we can carry out the numerical calculations for all values of x_0 .

Number of Quanta entering the earth's atmosphere.

The number of quanta given by (5') is distributed over a surface $4\pi d^2$, where d = distance of the earth from the sun. Hence the number n_ν whose energy exceed $h\nu$ entering unit surface of the earth's surface is given by

$$\begin{aligned} n_\nu &= 2\pi \left(\frac{R}{d}\right)^2 \cdot c \cdot \left(\frac{kT}{ch}\right)^3 \cdot I_1 \\ &= 2\pi\omega^2 \cdot c \cdot \left(\frac{kT}{ch}\right)^3 \cdot I_1. \end{aligned} \quad \dots (5)$$

NOTE 3

Energy of the Solar Radiation below a certain wavelength.

Let us denote by $E_\nu d\nu$ the radiation between the frequencies ν and $\nu + d\nu$. We have

$$E_\nu d\nu = \frac{8\pi^2 R^2}{c^2} \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu.$$

TABLE 8

Wave-length in Ångstroms	e-volts	$x = h\nu/kT$ $T = 6000^\circ\text{K}$.	$\frac{\log I}{I_1 = \int_x^\infty \frac{x^2}{e^x - 1} dx}$	$\frac{\log (I_2/6.494)}{I_2 = \int_x^\infty \frac{x^3}{e^x - 1} dx}$	Wave-length in Ångstroms	e-volts	$x = h\nu/kT$ $T = 6000^\circ\text{K}$.	$\frac{\log I}{I_1 = \int_x^\infty \frac{x^2}{e^x - 1} dx}$	$\frac{\log (I_2/6.494)}{I_2 = \int_x^\infty \frac{x^3}{e^x - 1} dx}$
23868.4	.517	1	0.3118	1.9843	1705	7.238	14	4.2740	4.6423
11934.2	1.034	2	0.1517	1.9130	1491	8.272	16	5.5137	5.9348
7956.1	1.551	3	1.9360	1.7837	1326	9.306	18	6.7414	5.2099
5967.1	2.068	4	1.6812	1.6053	1193	10.340	20	7.9595	6.4710
4773.6	2.585	5	1.3979	1.3896	1084.9	11.374	22	7.1698	7.7204
3977	3.102	6	1.0938	1.1457	994.6	12.408	24	8.3735	8.9599
3410	3.619	7	2.7731	2.8782	918.0	13.442	26	9.5716	8.1914
2977	4.136	8	2.4409	2.5936	852.4	14.476	28	10.7650	9.4159
2652	4.653	9	2.0955	2.2923	795.6	15.510	30	11.9544	10.6338
2386	5.170	10	3.7435	3.9795	745.8	16.544	32	11.1400	11.8472
2170	5.687	11	3.3838	3.6569	702.0	17.578	34	12.3225	11.0547
1989	6.204	12	3.01887	3.3258	663.1	18.612	36	13.5021	12.2584

Putting $h\nu/kT=x$, the required quantity is given by

$$\int_{\nu}^{\infty} E_{\nu} d\nu = 8\pi^2 R^2 \cdot \frac{k^4}{h^3 c^2} \cdot T^4 \cdot \int_{x_0}^{\infty} \frac{x^3 dx}{e^x - 1},$$

where $x_0 = h\nu_0/kT$; ν_0 is a certain minimum frequency. The total energy E_0 radiated by the sun is obtained by putting $x_0=0$. In this case, the integral $=\pi^4/15=6.494$. Let us denote by I_2 the integral

$$I_2 = \int_{x_0}^{\infty} \frac{x^3 dx}{e^x - 1}.$$

We have then

$$\frac{E}{E_0} = \frac{I_2}{6.494}.$$

The values of I_2 have been calculated and tabulated by Zanstra, and are shown in Table 8.

I have to thank my pupils Messrs. G. R. Toshniwal, L. S. Mathur and N. K. Saha for help in preparing the paper, particularly with respect to the mathematical calculation and preparation of Tables. The Deslandre-diagrams and the charts of N_2 and O_2 -levels are taken from a forthcoming paper by L. S. Mathur and P. K. Sengupta in the *Proceedings of the U.P. Academy of Sciences*.

REFERENCES

- ¹ Chapman, *Quarterly Journ. Roy. Met. Soc.*, vol. 52, p. 225 (1926). See also *Proc. Roy. Soc., A*, vol. 132, p. 353 (1931).
- ² Kirby and Judson, *Proc. Inst. Radio Eng.*, vol. 23, p. 733 (1935).
- ³ J. T. Henderson, *Can. J. Research*, vol. 8, Jan., 1933.
- ⁴ Chapman, *Proc. Phys. Soc. Lond.*, vol. 43, p. 26 (1931). Pedersen, Propagation of Radio waves round the Earth.
- ⁵ Appleton and Naismith, *Proc. Roy. Soc.*, vol. 150, p. 692 (1935).
- ⁶ Herzberg, *Ann. d. Phys.* (5), vol. 86, p. 189 (1928).
- ⁷ Slipher, *Mon. N.R.A.S.*, vol. 93, p. 665 (1933).
- ⁸ Sommer, *Zeits.f. Phys.*, vol. 51, p. 752, (1928) A; vol. 57, p. 582 (1929) B; vol. 58, p. 573 (1929) C; vol. 77, p. 377 (1932) D; vol. 80, p. 273 (1933) E; vol. 84, p. 269 (1934) F.
- ⁹ Dufay, *Journ. de Physique*, vol. 5, p. 523 (1934), and other papers.
- ¹⁰ Gauzit, *Journ. de Physique*, vol. 5, p. 523 (1934).
- ¹¹ Rosseland, *Astro. Journ.*, vol. 63, p. 218 (1926).
- ¹² Zanstra, *Astro. Journ.*, vol. 65, p. 50 (1927); *Pub. Dom. Astr. Obs.*, vol. 4, p. 209 (1931).
- ¹³ Beals, *Pub. Dom. Astr. Obs.*, vol. 4, p. 271 (1931).
- ¹⁴ Woolley, *Mon. N.R.A.S.*, vol. 94, p. 631 (1934); vol. 95, p. 101 (1935).
- ¹⁵ Minnaert, *Zeits. für Physik*, vol. 45, p. 610 (1927).
- ¹⁶ H. D. & H. W. Babcock, *Pub. Ast. Soc. Pacific*, vol. 46, p. 132 (1934).
- ¹⁷ Sommer, and Slipher, *Naturwissenschaften*, 1929, p. 802.
- ¹⁸ Götz and Meetham, *Proc. Roy. Soc., A*, vol. 145, p. 416 (1934).
- ¹⁹ Regener, *Phys. Zeits.*, vol. 35, p. 788 (1934).
- ²⁰ Vegard. The important series of publications of Vegard on the spectrum of the aurora are too numerous to be referred to in detail at every place. They are published in detail under the designation *Geophysical Publications of Norway, Oslo*. Shorter papers are to be found in the *Zeitschrift für Physik*, vol. 78, p. 574 (1932); vol. 89, p. 712 (1933).

59. SPECTRA OF COMETS

(*Sci. & Cult.*, 1, 476, 1936)

In a recent discussion on the ionosphere held under the auspices of the National Institute of Sciences, India, the writer of this note expressed the view that the ionization of the upper atmosphere and the spectrum of the night sky can be best explained if we suppose that the sun does not radiate like a black body in the ultraviolet, but sends out strong ultraviolet emission lines which can be identified with the resonance and other strong ultraviolet lines of He, He⁺, H, O... etc. Two lines of argument were cited in favour of this view; (1) that Slipher has established that the spectrum of the morning or evening flash gives strongly the band-spectrum of N⁺₂, even on days perfectly free from Aurora; (2) that the equilibrium of ozone formation requires that the number of quanta emitted between 3000 Å° and 2200 Å° must be as great as that between 2000 Å° and 1300 Å°.

Recently further corroboration of this view has been obtained in the spectra of comets. It is well known that

when comets are very far from the sun, they appear like a faint star (called the *nucleus*) which becomes enveloped in a kind of mist (*coma*) as the comet approaches the sun. With further approach to the sun, the comet develops a tail *i.e.* a long appendage which is held to consist of molecules repelled from the nucleus by the action of pressure of sunlight. With these characteristic changes in the appearance of the comet, it is observed that the spectrum also changes, the nucleus at a distance shows a continuous spectrum crossed with Fraunhofer lines showing that the comet consists of meteorites and the continuous spectrum is due to reflection of sunlight from these. When the comet approaches closer, the meteorites get heated and evolve gas. The spectrum of the coma shows emission bands due to CN, C₂ (Swanbands) CH (doubtful). Zanstra thinks that these emission bands are due to absorption of sunlight by the vapour in the coma and subsequent re-emission just as in his well-known theory of nebular luminosity. The

tail shows lines due to ionized CO^+ , and ionized N_2^+ (second negative bands).

The excitation potential of the N_2^+ band has been definitely proved to be 21.10 and that of CO^+ bands (comet tail bands) is *ca* 17 e.volts. It is clear (for further details, reference may be made to the author's forthcoming paper in the *Proc. Nat. Inst. Sci.*) that if we regard that sun radiates like a black body at a temperature of 6000°K , there is not sufficient number of ultraviolet quanta of the proper frequency which can produce the observed ionization of the cometary gases N_2 and CO . In fact, it was shown

that most probably the resonance line of He are responsible for the ionization of N_2 to N_2^+ (excited) in the upper atmosphere. The same can be said of the cometary phenomenon. The observed ionization of N_2 to N_2^+ in the comet tail and that of CO to CO^+ may be supposed to be due to the ultraviolet emission lines of He and other elements from the sun.

Department of Physics,
Allahabad University.

4.12.1935

60. CAN ELECTRONS ENTER THE NUCLEUS

(*Sci. & Cult.*, 2, 273, 1936)

A number of experiments have been performed of late to find out whether high energy electrons can be made to enter the nucleus, but with no definite result. The maximum potential so far applied has been 800 K Volts (See *Phys. Rev.*, 1935). The failure of these experiments is not difficult to understand, as the de-Broglie wavelength is nearly 100 times larger than the diameter of the nucleus.

But from these experiments, it is not safe to assume that the electron can never enter the nucleus. In fact, the uncertainty principle enables us to find out the energy which the electron must have in order that it may enter the nucleus: if we wish to accommodate a particle in a space of dimension ' l ', the uncertainty in its momentum is given by

$$\Delta p \text{ nearly} = \frac{h}{l}.$$

Putting $l = a \cdot 10^{-13}$ cm (dimension of the nucleus) we have Δp

$$\text{nearly} = \frac{h}{a \cdot 10^{-13}}$$

$$\text{nearly} = \frac{6.54}{a} 10^{-14} \text{ gm} \times \text{cm}.$$

Now $\Delta p < p < mc$, where m is the relativity-mass of the electron. We have therefore

$$mc > \frac{6.54}{a} 10^{-14} \text{ gm} \times \text{cm} \text{ or } \frac{m}{m_0} > \frac{2.4}{a} 10^3.$$

Taking a nearly $= 2.4$ (diameter of the N-nucleus), we find that electrons can enter the nucleus if

$$\frac{m}{m_0} \text{ nearly} = 10^4,$$

i.e., the energy is nearly 5×10^9 e volts. Now electrons of such high velocity are found in cosmic rays and it can be easily shown that in course of their passage through the atmosphere a good fraction of them must suffer nuclear collisions. The number of such collisions can be easily calculated. It is given by

$$\pi a^2 (10^{-13})^2 \times 2.8 \times 10^9 \times z = 1.8 \times 10^{-6} z,$$

where z is the equivalent height of the atmosphere through which the electron has passed. Even at a height of 30 Km, the electron, at vertical coincidence, has passed through 65 meters of air, *i.e.*, suffered 1.17×10^{-2} nuclear collisions *i.e.*, one electron in a hundred suffers a nuclear collision—on the sea level, the number of nuclear collisions would be about 1.5, *i.e.*, even at a height where the pressure is $\frac{2}{3}$ the atmospheric pressure (5 kms), the primary electron must have passed through the nucleus. This incident cannot be without influence on the general cosmic ray phenomenon.

The effect of the entry on the nucleus would probably be to explode the nucleus, and give rise to secondaries.

15.8.1936

61. THE ORIGIN OF MASS IN NEUTRONS AND PROTONS*

(*Ind. Journ. Phys.*, **10**, 141, 1936)

(Received for publication, March 2nd, 1936.)

1. INTRODUCTION

The use of 'mass' as a fundamental concept dates from the time of the rise of Galileo-Newtonian mechanics, but discoveries in physics within the last sixty years have shown the necessity of our revising the original concept. As early as 1885, J. J. Thomson showed from classical electrodynamics that a spherically charged body moving with a velocity v has its energy increased by the amount $\frac{2\mu e^2}{15 ac^2} v^2$, where a is the radius of the sphere and μ is the permeability of the medium. The arguments used were rather of a hydrodynamical nature. These studies were further continued by H. A. Lorentz and others and brought to a close by Abraham. These results may be quoted here. When a sphere of radius a charged with the electricity ' e ' moves with a velocity v , which is small compared to the velocity of light, it produces in the space,

$$\left. \begin{aligned} \text{the } e.m. \text{ energy} &= \frac{1}{3} \frac{e^2}{ac^2} v^2, \\ \text{the } e.m. \text{ momentum} &= \frac{e^2}{ac^2} v. \end{aligned} \right\} \dots (1)$$

We can say that the mass has increased by $m = \frac{2}{3} \left(\frac{e^2}{ac^2} \right)$ when we calculate it from the energy value. When, however, we calculate it from $e.m.$ momentum, the mass increment comes out to be $\frac{e^2}{ac^2}$. The explanation of this discrepancy has not been forthcoming.

When v is comparable to the velocity of light, Lorentz showed that if we suppose that the length of the sphere is reduced in the ratio of $\sqrt{1-v^2/c^2}$ we get

$$\text{The } e.m. \text{ energy} = \frac{1}{3} \frac{e^2}{ac^2} \frac{v^2}{\sqrt{1-v^2/c^2}} \dots (\text{Hypothesis of contractile electron})$$

Thus the increment in that part of the mass which is of electromagnetic origin follows the law, $m = m_0/\sqrt{1-v^2/c^2}$. When these theories were being developed, Kaufmann and J. H. Thomson showed experimentally that the mass of

the electron increases with velocity and later experiments have shown that the variation is governed by the law

$$m = m_0/\sqrt{1-v^2/c^2}. \dots (3)$$

This proved that the whole mass is of electromagnetic origin, and we are justified in saying that the electron has a radius

$$a = \frac{2}{3} \frac{e^2}{mc^2} \text{ or } = \frac{e^2}{mc^2},$$

according as we take the energy or the momentum for determining the mass.

Hypothesis of Rotating Electrons.

Abraham showed that if the spherical charge be supposed to rotate with the angular velocity ω it can be shown to possess the following properties:—

$$\left. \begin{aligned} \text{Rotational energy} &= \frac{1}{9} \frac{ae^2}{c^2} \omega. \\ \text{Mechanical moment} &= \frac{2}{9} \frac{e^2 a}{c} \omega. \\ \text{Magnetic moment} &= \frac{a^2 e}{3c} \omega. \end{aligned} \right\} \dots (4)$$

Since the moment of inertia of a hollow spherical body of mass m about any diameter $= \frac{1}{2} ma^2$, the angular momentum $= \frac{1}{2} ma^2 \omega$. We have, equating the two

$$m = \frac{2}{3} \frac{e^2}{ac^2}. \dots (3')$$

Identity of Mass and Energy.

In the meantime, Einstein, proceeding from the assumptions of invariance of form of equations of motion when referred to two space-time co-ordinate systems moving with respect to each other with the velocity v , had arrived at the conclusion that energy and mass are identical, being connected by the expression

$$E = mc^2, \dots (5)$$

where c = velocity of light. When the units of time and space are so chosen that $c=1$, E becomes identical with m .

* Address delivered before the Indian Physical Society on 8th February, 1936.

This theorem, which forms the corner stone on which all studies of nuclear reactions have been based, is independent of any hypothesis except the general assumption underlying the special theory of relativity. It is, however, in agreement with the Lorentz theory of electromagnetic origin of mass, as the variation of mass is given by

$$m = m_0 / \sqrt{1 - v^2/c^2}.$$

In fact, if we accept this theorem, then to calculate the mass of any fundamental particle (electron, proton, etc.), we have to find out its energy of formation. This, when divided by c^2 , gives us the mass of the particle.

Mass of the Electron and the Proton.

The energy of formation of a spherical charge e distributed over a sphere 'a' is given by $\frac{e^2}{2a}$ and hence its mass is $\frac{1}{2} \frac{e^2}{ac^2}$ but it is usual to multiply it by 4/3 which is supposed to represent the action of forces which prevent the electron from exploding. We have no method of knowing a directly, but as e and m are known, it is customary to use the term "electronic radius" to denote the quantity $\frac{2}{3} \frac{e^2}{mc^2}$, or omitting $\frac{2}{3}$, simply to denote $\frac{e^2}{mc^2}$ as the electronic radius. Its value is

$$\frac{e^2}{mc^2} = 2.83 \times 10^{-13} \text{ cm.}$$

and we have

$$\frac{e^2}{mc^2} = \frac{h^2}{4\pi^2 e^2 m} \left(\frac{2\pi e^2}{ch} \right)^2 = r\alpha^2, \quad \dots (6)$$

where r = fundamental Bohr radius, and α = Sommerfeld fine-structure constant.

The difficulties in the above theory of origin of mass have not yet been overcome; in fact they have been accentuated after the rise of quantum mechanics, and increase in our knowledge of the physical properties of the electron.

§ 2. THE MASS OF THE PROTON

Before 1932, the other fundamental particle was the proton.

The task of the accounting for the mass of the proton on the above basis presented greater difficulty. It had to be assumed that the radius of the proton is nearly 1847 times smaller, i.e., nearly 10^{-16} cm. While there is nothing against the hypothesis of such a small diameter for the proton, it does not help us much, for it merely accepts the situation; the reason why the proton mass is so much heavier than the electron, though the charge is the same, remains unexplained.

In recent years, the discovery of the neutron has put the whole question in a new light and has shown that the energy of formation of the proton cannot be of electrical origin alone. The neutron has no electrical charge; still it has a mass which is 1852 times heavier than that of the electron. If we wish to account for the mass of the neutron, we can no longer seek for its origin in the electromagnetic theory as the neutron is uncharged. We have, therefore, to calculate its energy of formation in a different way from that of the electron. When we have been able to account for the mass of the neutron, that of the proton may be next attempted, as the proton is most probably a neutron which has lost an electron or a neutron which has acquired a positron.

Mass of the Neutron.

According to the recent measurements, the neutron is $1847 \times \frac{1.084}{1.081} = 1852$ times heavier than the electron. It has a spin of $\frac{1}{2}$ and obeys, as Heisenberg has shown, Fermi-Dirac statistics. We cannot say what its magnetic moment in the free state is, but in the nucleus its magnetic moment is certainly of the same order as that of the proton. This is proved by two known results. The nitrogen nucleus N^{14} is most probably composed of three α -particles, one proton and one neutron. Its spin is known from measurements of intensity data of N^{14} bands to be one. But Bacher has shown that lines of N show no hyperfine structure. Hence the magnetic moment of the nucleus is zero. Now the α -particles have their spin = 0 and magnetic moment = 0 and therefore, we have to assume that the proton and the neutron have their spin in the same direction, but their magnetic moments cancel each other, i.e., the neutron behaves like the anti-proton as far as the magnetic moment is concerned. The spin and the magnetic moment of the deuteron tell us the same story. The spin is one, but the magnetic moment has been found to be .4 times that of the proton viz, $\frac{5}{2} \frac{eh}{4\pi cM}$, hence that of the neutron is $\frac{3}{2} \frac{eh}{4\pi cM}$, where M is the mass of the proton.

3. FREE MAGNETIC POLES

It was Dirac¹ who first showed that quantum mechanics demands the existence of free magnetic poles, having the pole strength (or magnetic charge) $\frac{ch}{4\pi e} = \frac{e}{2\alpha^2}$ where α = Sommerfeld fine-structure constant. Recently, the present author deduced the existence of free magnetic poles from very simple considerations. If we take a point charge e' at A and a magnetic pole μ at B, classical electrodynamics tells us that the angular momentum of the system

$$A. \frac{e}{(e)} \cdot B. \frac{B}{(\mu)}$$

about the line AB is just $e\mu/c$. Hence, following the quantum logic, if we put this $= \frac{1}{2} \frac{h}{2\pi}$, the fundamental unit of angular momentum, we have $\mu = \frac{hc}{4\pi e} = \frac{e}{2\alpha}$, which is just the result obtained by Dirac.

Spin and Mass of the Magnetic Particle.

But the concept of a fundamental particle requires that we should have also precise knowledge about their rest-mass, their spin, as well as the statistics they obey.

Mass of the Free Magnetic Poles.

We can calculate the mass of the free magnetic poles in the same way as for electric charges by using classical electrodynamics. It is useless to repeat the mathematical working. If the poles are spherical, and the magnetic charges are distributed over a radius b we have the mass M given by

$$M = \frac{2}{3} \frac{\mu^2}{bc^3} = \frac{2}{3} \frac{e^2}{bc^3} \frac{1}{4\alpha^2} \quad \dots (7)$$

Thus the ratio of the mass of the magnetic poles to that of the electron is

$$\frac{M}{m} = \frac{q}{b} \frac{1}{4\alpha^2} \quad \dots (8)$$

We have no method of determining b as the free magnetic pole is still undiscovered and its mass is not known. But let us assume with Eddington² that the radius of fundamental particle in the sense used here, is given by some universal principle and is the same for all particles. Thus we take $a=b$. We have then

$$\frac{M}{m} = \frac{1}{4\alpha^2} = \frac{(137.29)^2}{4} = 4712.1. \quad \dots (9)$$

Thus on these assumptions the free magnetic pole is $4712/1852=2.540$ times heavier than the neutron. Its radius is now $r\alpha^2$, where α =Sommerfeld constant, and r is the fundamental Bohr radius. The objection may legitimately be raised against the hypothesis that the radius of the *Magnetron* (free magnetic pole) should be the same as that of the electron, but if we assume a smaller radius, the particles become proportionately heavier. The existence of such heavy particles is not yet known.

Why have we not been able to observe the free magnetic pole?

This question was tackled by Dirac. He thinks that the force of attraction between the poles is so great, that in Nature, a positive and a negative pole always occur in pairs forming a dipole, secondly, Tamm³ tried to calculate the 'eigen'-energy of a system consisting of a free magnetic pole and an electron. No 'eigen'-values were found, but

it was pointed out by the present writer that the assumptions underlying these mathematics were probably faulty.

Identification of Magnetic Dipoles with Neutron.

It was suggested by D. S. Kothari⁴ that the neutron or the skeleton of it, may possibly be the dipole composed of two equal and oppositely charged free magnetic poles. This suggestion may be given a trial. As we have already shown, the magnetic moment of the neutron is of the order $\frac{eh}{4\pi Mc}$ and let us suppose that it is given by

$$J = \frac{eh}{4\pi Mc} \theta = l. \mu, \quad \dots (10)$$

where l =distance between the centres of the two poles. We get

$$l = \frac{e^2}{M_p c^2} = \frac{e^2}{mc^2} \times \frac{m}{M_p} = a. 4\alpha^2 = 4r\alpha^4. \quad \dots (11)$$

Thus while we assume the dimensions of the magnetic poles to be of the order of $r\alpha^2$, the distance of their centres when they form dipoles appears to be of the order $r\alpha^4$ i.e., α^2 -times less. Let us see whether we can obtain any justification for this apparent contradiction.

The Dirac Equations for Free Magnetic Poles.

For this purpose, we can study a system consisting of two Dirac oppositely charged poles. Let their masses be M_p and the magnetic charge be μ . Our problem is to write out the relativistic Dirac Equations for the system and to find out 'eigen'-values.

This is a problem of two bodies, for which special relativity has as yet found no solution, as each particle has its own individual space and time. But we can reduce the present problem to a one body one, by assuming that the bodies are always at the opposite ends of a diameter passing through the centre of gravity, and their motions are equal and opposite. We can also formulate the equations of motion in the same way as in the case of the electron, only we have to use $\frac{e}{2\alpha}$ for e , and the potential four-vector is now the magnetic potential four-vector, i.e., they act upon a magnetic pole.

We have $\mathbf{a}_x = \mathbf{a}_y = \mathbf{a}_z = 0$

and $\mathbf{a}_1 = -\frac{i\mu}{2r}$;

hence the potential energy $= -\frac{\mu^2}{2r} = -\frac{e^2}{8\alpha^2 r}$ where r is the distance of any particle from the C. G.

The equations of motion for one particle can therefore be written as:—

$$\frac{i}{hc} \left(E + \frac{e^2}{8\alpha^2 r} + E_0 \right) U_1 + \frac{dU_3}{dz} + \frac{dU_4}{dx} - i \frac{dU_4}{dy} = 0. \quad \dots (12)$$

and three other similar equations. (For the notation, see, Bethe, Handbuch der Physik, 24, p. 311.) $\left(h = \frac{h}{\pi}\right)$.

We have $E_0 = M_{p_0}c^2$, $E = M_p c^2$

where M_{p_0} is rest mass of the particles $= m/4\alpha^2$,

M_p = mass under present conditions, which we have to calculate.

As shown by Bethe, the equations can be reduced to the forms:—

$$\frac{dF}{dr} - K \frac{F}{r} = \left[\frac{M_0 c}{h} \left(1 - \frac{E}{E_0}\right) - \frac{1}{8\alpha r} \right] G, \quad \dots (13)$$

$$\text{and } \frac{dG}{dr} + K \frac{G}{r} = \left[\frac{M_0 c}{h} \left(1 + \frac{E}{E_0}\right) + \frac{1}{8\alpha r} \right] F.$$

Our F is Bethe's χ_1 , G is his χ_2 .

The equation differs from (9-12) of Bethe's only in having $M_0 = m/4\alpha^2$ in place of m in Bethe's and in place of α which is $\frac{1}{137.29}$, we have $\frac{1}{8\alpha} = \beta = 17.16$.

We thus find that β is no longer a small quantity but is equal to 17.16.

We have also

$$\frac{Mc}{h} = \frac{mc}{h} \cdot \frac{1}{4\alpha^2} = \frac{1}{4a\alpha^3}. \quad \dots (14)$$

For solving this equation, let us put $F = Ae^{-\lambda r}$, $G = Be^{-\lambda r}$ and $\lambda = \frac{M_0 c}{h} \sqrt{1 - \epsilon^2}$ where $\epsilon = \frac{E}{E_0}$ and we introduce a new variable $\rho = 2\lambda r$.

Then the equations reduce to

$$\frac{dA}{d\rho} - \frac{A}{2} - \frac{k}{\rho} A = \left[\frac{c}{2} - \frac{\beta}{\rho} \right] B \quad \dots (15)$$

$$\frac{dB}{d\rho} - \frac{B}{2} + \frac{k}{\rho} B = \left[\frac{1}{2c} + \frac{\beta}{\rho} \right] A,$$

$$\text{where } c = \sqrt{\frac{1-\epsilon}{1+\epsilon}}.$$

This equation can be solved exactly as in Bethe's article, by the polynomial method, and we obtain,

$$c = \frac{1}{\sqrt{1 + \left(\frac{\beta}{n_r + \sqrt{k^2 - \beta^2}} \right)^2}}. \quad \dots (16)$$

We have $\beta = \frac{1}{8\alpha}$ but unfortunately there is at present great divergence of opinion regarding the exact value of $\alpha = 2\pi e^2/ch$ as the values of c , h and particularly of e obtained from different experimental methods, do not agree within reasonable limit. Birge has discussed the problem in a recent note to the Physical Review (Vol, 48, 1935). If we follow his directions, $1/\alpha$ is found to vary between 137.29 to

136.26. If $\alpha = \frac{1}{136}$, β would be exactly 17, but if it is 137.29, $\beta = 17.16$: it is not an integral number. But k must be integral and $\geq \beta$.

If $\beta = 17$, we could have put $k = \beta$ and $n_r = 0$ we would get $\epsilon = 0$, i.e., this would correspond to the case of complete annihilation; the whole mass energy is given out as radiation.

But there is very little likelihood that $\beta = 17$; we take $\beta = 17.16$ and k can be given integral values > 17 . If $k = 18$ and $n_r = 0$ we obtain,

$$\epsilon = .302.$$

i.e., the mass of the dipole is now reduced to $2 \times .302 \times \frac{1}{4\alpha^2} = 2846$ -times the mass of the electron $= 1.52$ -times the mass of the neutron. Thus the mass-ratio does not come out correctly. When $k > 18$ and tends to infinity, ϵ tends to unity.

The ψ -functions for the above solution have their maximum value at

$$r = \frac{\sqrt{k^2 - \beta^2} - 1}{\lambda} = 4a\alpha^3 \{ \sqrt{2\beta + 1} - 1 \}, \quad \dots (17)$$

i.e., at distances of the order of $4a\alpha^{\frac{5}{2}}$ since $\beta = \frac{1}{8\alpha}$. Thus the nuclear distance does not come out to be of the order $a\alpha^4$ as demanded by physical considerations, but is much larger.

The solutions we have treated are real only for $k > \beta$ but it is just possible that we may have solutions which hold for $k < \beta$ but a search for such solutions has not yet yielded any positive result.

4. A REVIEW OF OTHER ATTEMPTS FOR EXPLAINING THE PROTON-ELECTRON MASS RATIO.

It is now recognised that the explanation of the proton-electron mass ratio forms one of the outstanding fundamental problems of physics, and in recent years, a number of attempts has been made by distinguished scientists to solve it.

Sir A. S. Eddington published between 1929 and 1932 a number of papers in the Proc. Roy. Soc. on this subject. He believes that $\frac{1}{\alpha} = \frac{ch}{2\pi e^2}$ is exactly 137 and $136 = 137 - 1$

represents the number of degrees of freedom of the Dirac-electron; and that 10 represents the number of degrees of freedom of a particle in Riemannian space. From these assumptions he writes out the following equations for particles in Riemannian space:—

$$\left\{ 10 \left(iE_s \frac{\partial}{\partial \theta_s} \right)^2 + 136 \left(iE_s \frac{\partial}{\partial \theta_s} \right) + 1 \right\} \psi = 0. \quad \dots (18)$$

The mass m of the particle satisfying this equation is given by the roots of

$$10m^2 - 136m + 1 = 0. \quad \dots (19)$$

The ratio between the two roots is 1847.60 which is almost the proton electron mass-ratio.

No comment is needed on this interesting speculation, but physicists will probably like to have some theory which will make a more direct appeal to their experience.

The second attempt has been made by Born and Pryce. They suppose that the proton and the positron are different quantum states of the same particle, the positron being defined by $s=\frac{1}{2}$, $l=0$, $j=\frac{1}{2}$ and the proton by $s=\frac{1}{2}$, $l=1$, $j=\frac{1}{2}$. The analogy to the Goudsmit-Uhlenbeck explanation of the states of the H-atom is apparent. The spin motion is supposed to give rise to the electrostatic energy formation, viz., $\frac{2}{3} \frac{e^2}{a}$, or rather Born and Infeld's modification

of the above expression in which the difficulty of an infinite energy with $a=0$ is avoided. In the state $l=1$, $s=\frac{1}{2}$ the particle receives an increment of energy due to the l -motion, which is identified with the mass of the proton. This is calculated as follows:—The motion endows the particle with the magnetic moment $l \frac{eh}{4\pi m^2}$ or since $l=1$ with the moment $\frac{eh}{4\pi m^2}$. This gives rise to a rotating magnetic field in space. If this body be supposed to be a sphere of radius a , the energy of the field is $\frac{1}{2} \frac{\mu^2}{a^3}$ on the analogy of classical electrodynamics. We find therefore the energy of formation of the particle

$$Mc^2 = \frac{1}{2} \frac{\mu^2}{a^3} = \frac{1}{2} \left(\frac{eh}{4\pi m^2} \right)^2 \frac{1}{a^3} = \frac{1}{2} \frac{e^2}{4\pi^2} \cdot \frac{1}{a}.$$

$$\text{Since } \frac{e^2}{mc^2} = a, \text{ we have } \frac{M}{m} = \frac{1}{8\pi^2} = 2340. \quad \dots (20)$$

The experimental value is 1847.

Born is of opinion that though the ratio has not come out correctly, the investigation has made it clear that the ratio M/m should be a simple function of the Sommerfeld fine-structure constant.

In spite of the great ingenuity displayed in the above working, it is doubtful whether the theory will carry much conviction. First, the identification of the energy of s -motion with electrostatic energy will find few supporters amongst physicists and is opposed to the accepted explanation of s -motion. Secondly, there is no experimental evidence that the positron and proton are different quantum states of the same particle. It will be noticed that *the neutron is altogether ignored* in this investigation. Thirdly, the calculation of energy of formation has been made only for $s=\frac{1}{2}$, $l=1$. But what about the states $l=2, 3, \dots$? On the above

logic, they are likely to give rise to nuclei of masses $2^2, 3^2, \dots$ times that of the proton. No experimental evidence has yet been found for the existence of such nuclei.

Another objection is that the magnetic moment of the proton has been observed by Stern and Eastermann to be $\frac{5}{2} \frac{eh}{4\pi cM}$ and this is about $\frac{1}{750}$ times the moment ascribed to the l -motion of the particle, viz., $\frac{eh}{4\pi cm}$. Born says

that this moment is due to s -motion which is also $\frac{eh}{4\pi cm}$, but acts in the opposite direction, leaving a small residue $5/2 \frac{eh}{4\pi cM}$. But the assumption is frankly arbitrary, and further it is illogical to regard ' s ' as being of electrostatic origin and then to suppose that it gives rise to a magnetic moment.

While criticising other views, it is not the author's intention to conceal the insufficiency of his own investigation. First, the mass ratio has not come correctly. This may be partly due to a faulty formulation of the problem of relativistic wave-mechanics of two bodies, and partly due to the fact that the Dirac equation has other solutions which have not yet been discovered. But a more potent reason seems to be the assumption that the magnetostatic attraction between the two particles is given by the law of inverse square. The size of the particles has been assumed to be of the order $r\alpha^2$, whereas the nearest distance of approach when the particles from a neutron is of the order $r\alpha^4$. Hence it appears that we shall have to assume a different law of attraction. Besides, we have to account for the spin-value, the magnetic moment and the statistics obeyed by the dipole. The spin of the free magnetic pole is probably zero, for we have assumed that the spin of the combination magnetic pole-electron is $\frac{1}{2}$ about the joining line AB, while that of the electron is also $\frac{1}{2}$. Considerations of equilibrium also require that the electron axis would be parallel to the line joining the two particles. Hence the spin of the magnetic pole should be zero.

It is doubtful, if the spin of the free magnetic pole be zero, whether Dirac's equations of motions can be applied to it, for in Dirac's theory, the resultant angular momentum which comes as an integral of the equations of motion is always half-valued. The other possibility is Schrödinger's treatment of the relativistic wave equation, but even this does not give us the correct result.

The only positive result is that the large value of the mass-ratio M/m is ascribed to the fact that the mass of the neutron arises from an entirely different cause than the mass of the electron. It is due to free magnetic poles.

The whole investigation is based upon the tacit assumption of the existence of free magnetic poles and since these have not yet been discovered, we have to show that they are not figments of the imagination. Their existence has

been deduced from straightforward quantum logic, and hence it is difficult to throw doubt on their existence. We rather discuss why the poles have not so far been discovered. According to our hypothesis the magnetic poles can never occur in free state in our universe. When two magnetic poles combine to form a neutron, nearly eighty per cent. of the energy is radiated away in the form of radiation of energy 3.7×10^9 e. volts, hence it is almost impossible to split up the neutron. It is just possible that when a neutron lying within a nucleus is bombarded by a cosmic ray of suitable energy, it is split up into free magnetic poles which produce intense disturbance in the nucleus as they are liberated. May not the mysterious phenomena of cosmic ray *bursts* be due to this cause?

I wish to express my thanks to Dr. D. S. Kothari, and Mr. Ramnivas Rai, with whom the contents of the paper were discussed.

[Note added:—In course of a discussion on the paper, Prof. D. M. Bose raised the point that if the same mathematics were to be applied to the motion of a positron and electron about each other, we should get corresponding solutions, where 80% of the mass would be radiated away. We know of no such radiation or of particles. I have since given some thought to Prof. Bose's point but

find that the electron-positron case cannot give rise to the kind of solutions contemplated by Prof. Bose. For we should have

$$\epsilon = \frac{1}{\sqrt{1 + \left(\frac{\alpha/2}{\sqrt{n_r + k^2 - \alpha^2/4}} \right)^2}}, \quad (A)$$

where $\frac{\alpha}{2}$ takes the place β in (16). Now β is a large number > 17 , while $\frac{\alpha}{2}$ is a small fraction. The lowest allowable value of k in (A) is unity. It may be easily verified that this leads to values of $\epsilon = 1 - \frac{\alpha^2}{8n^2}$, $n = n_r^2 + k$, and the radiation emitted is

$$\nu = \frac{Ry}{2} \left(\frac{1}{n^2} - \frac{1}{n'^2} \right),$$

i.e., they should have double the wave-length of ordinary hydrogen lines. Such lines were looked for in the spectrum of the corona (see Observatory, 56), but none has been so far obtained.]

REFERENCES

- ¹ Dirac, *Proc. Roy. Soc., A*, **133**, 60 (1931).
- ² Eddington, *Proc. Roy. Soc., A*, **133**, 605 (1931); **134**, 524 (1931); **138**, 17 (1932).
- ³ Tamim, I. *Zeits f. Phys.*, **71**, 141 (1931).
- ⁴ Kothari, a private communication.

62. A CRITICAL REVIEW OF THE PRESENT THEORIES OF THE ACTIVE MODIFICATION OF NITROGEN

M. N. SAHA AND L. S. MATHUR

(*Proc. Nat. Acad. Sci., Ind.*, **6**, 120, 1936)

(Received December 10, 1935)

All the existing theories regarding the phenomenon of Active Nitrogen have been criticised in the present paper and the authors have tried to show the inadequacy of each one of them. It is concluded that atomic nitrogen has nothing to do with the active modification and the experiments which establish its presence are not correctly interpreted. It is shown that the long life of the afterglow which is about 5½ hours according to the recent experiments of Lord Rayleigh throws a new complexion on the phenomenon. It is thought that in Active Nitrogen the molecule is raised to some state composed of two ²D atoms and probably located at 9.77 volts.

The first attempt at a theoretical explanation of the phenomenon of Active Nitrogen was made by the senior author and Dr. N. K. Sur¹ of this laboratory in 1926; they thought that ordinary unexcited molecules of Nitrogen are excited by a discharge to an energy which they

estimated to be about 8.5 volts. This excited molecule was supposed to have a very long life and when it collides with a foreign molecule or an atom, then it transfers this energy to the second particle by collisions of the second type. The second molecule or atom is thereby excited to emit its spectrum or become chemically reactive. In this way they attempted to explain many of the results obtained by E. P. Lewis², Fowler and Strutt³.

At the time when this suggestion was made our knowledge of the energy levels of the Nitrogen atom and the molecule was practically non-existent and this suggestion stimulated an extraordinary amount of activity on the subject. All these works gave rise to further theories or modifications of Saha and Sur's theory. In view of these works, and the

great advance in our knowledge of the spectrum of the N atom and the molecule¹ it is possible now to take a critical review of these theories.

Birge⁵ held that the energy of the metastable molecule was not 8.5 volts as then considered by Saha and Sur but 11.4 volts, a value which is now known to be rather wide off the mark. The next theory was that of Spomer⁶ and is now known as the *triple collision theory*. In this it is supposed that by the discharge, the Nitrogen molecule is split up into free atoms. The afterglow is produced when two atoms recombine and the energy of recombination is delivered over to a third molecule which happens to be present at the point of collision. This hypothesis explains to some extent the long life of the afterglow as well as the experimentally observed fact that the decay of the afterglow is not a monomolecular, but either a bi- or tri-molecular reaction. The basis of Spomer's assumption was that the *energy of dissociation of the normal Nitrogen molecule into two 4S atoms is 9.5 volts*, a value which was favoured by the knowledge of the molecular spectrum of N_2 available up to that time. It has now been found that this value is too high, for Herzberg⁷ has proved that the heat of dissociation of N_2 into two 4S atoms is 7.34 volts.

In 1929, the above theory was modified by Cario and Kaplan⁸ who assumed that Active Nitrogen contains a mixture of metastable molecules of Nitrogen in the $A\ ^3\Sigma$ state, and metastable atoms in 2P and 2D states, whose

Table 1. Energy in volts of the vibrational levels of the States $A\ ^3\Sigma_g^+$ and $B\ ^3\Pi_g$ of N_2 .

A-level				B-level	
v	V_A in volts	$V_A + ^2D$ in volts	$V_A + ^2P$ in volts	v	V_B in volts
0	0.00	2.37	3.56	0	1.18
1	0.18	2.55	3.74	1	1.39
2	0.35	2.72	3.91	2	1.59
3	0.52	2.89	4.08	3	1.70
4	0.68	3.05	4.24	4	1.99
5	0.84	3.21	4.40	5	2.19
6	1.01	3.38	4.57	6	2.38
7	1.16	3.53	4.72	7	2.57
8	1.31	3.68	4.87	8	2.76
9	1.46	3.83	5.02	9	2.94
				10	3.12
				11	3.29
				12	3.46
				13	3.63

excitation energies are 3.56 and 2.37 volts respectively. It was thought that molecules in $A\ ^3\Sigma$ state are excited to $B\ ^3\Pi$ state with $v'=10, 11$, and 12 by collisions with 2P and to the state $v'=6$ by collision with the metastable atom 2D . This point is well illustrated in table 1.

From table 1, it will be seen that in the zero vibrational level of the $A\ ^3\Sigma$ metastable state will be raised to the $B\ ^3\Pi$ state with $v=6$ or 12 by coming in collision with 2D and 2P atoms respectively. Thus these bands will be enhanced, as was actually found to be the case in the experimental work of Kichlu and Acharya,⁹ Herzberg Spomer and others.

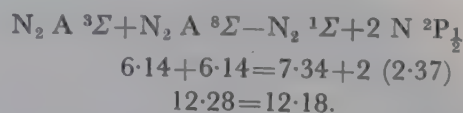
At the time when this theory was propounded, the energy value of the A-level was supposed to be 8.1 volts, so that the energy of the level B_{12} to which the nitrogen molecule was raised by collision with the nitrogen 2P atom was 11.56 volts, that of the B_6 level which is produced by collision with the 2D atoms would be 10.48 volts. Now, the energy content of the Nitrogen molecule which by collision of the second type excites atoms to the emission of their characteristic light has been determined with great care by Okubo and Hamada.¹⁰ They find this energy to be 9.51 volts. The active molecules present in active modification of Nitrogen in the original theory of Cario and Spomer are

$$8.1\ (A\ ^3\Sigma),\ 10.48\ (B_6\ ^3\Pi)\ \text{and}\ 11.56\ (B_{12}\ ^3\Pi).$$

In none of the atomic reactions so carefully observed by Okubo and Hamada special excitation of any line corresponding to any of the above energy values is noticeable¹¹.

It is now known from the discovery of Vegard-Kaplan¹² bands that the energy of excitation of $A\ ^3\Sigma$ state is 6.14 volts. When this became known Cario¹³ modified his theory. The energy values of the molecular states now come to be 6.14 ($A\ ^3\Sigma$), 9.60 ($B_{12}\ ^3\Pi$), produced by collision with 2P atoms and ($B_6\ ^3\Pi$) produced by collision with 2D atoms. The authors pointed out that the energy of the B_{12} state is just the same which is obtained in the experiments of Okubo and Hamada.

They further pointed out that the metastable atoms $^2P_{\frac{1}{2}}$ would be generated even in the absence of a discharge by impact of two $A\ ^3\Sigma$ molecules as shown below:—



But 2D atoms cannot be produced by this process, and the authors suppose that there are more 2P atoms in the active modification than 2D atoms.

In support of this theory Cario and Kaplan argue that the presence of atomic nitrogen in the active modification is supported by the experiments of Wrede¹⁴ and Broadway and Jackson.¹⁵ We wish, however, to point out that a critical review of these experiments shows that proper

interpretation has not been put on them. A short account of these experiments which is given below will illustrate this point.

Wrede passes through a discharge tube a steady stream of Nitrogen so that the pressure is maintained constant. There are a number of side-tubes and through a diffusion plug inserted in one of these, the gas in the discharge tube is allowed to diffuse to another tube where, if no discharge passes, the pressure would have the same value as in the discharge tube. If the discharge is allowed to pass, the pressure and temperature on the two sides of the diffusion space varies. The change in pressure can only be due to the fact that some of the molecules are broken up by the discharge into atoms and diffuse faster into the other tube where they recombine to form molecules. Let p_o , T_o be the pressure and temperature in the absence of the discharge and p_e , T_e the corresponding quantities when the discharge is passed. Then it can be shown that the partial pressure of atomic Nitrogen in the discharge tube is given by

$$\frac{p_A}{p_e} = \frac{1 - \frac{p_o}{p_e} \sqrt{\frac{T_e}{T_o}}}{0.293}.$$

Wrede actually found that about 20 to 30% of atomic nitrogen is produced in the discharge tube under favourable conditions. We accept this result, but wish to remark that the experiment merely proves that, molecules are broken up into atoms in the discharge space. It does not, however, prove that free atoms persist in the afterglow space. In fact, recent experiments of Lord Rayleigh,¹⁶ which show that active nitrogen, segregated in a discharge-free space can continue to glow for $5\frac{1}{2}$ hours, absolutely disprove that atomic nitrogen is responsible for active nitrogen phenomena. Any free atom produced in the excited state will die out in course of 10^{-8} sec. and a metastable atom will revert to the normal 4S state at most in 10^{-1} sec. Free Nitrogen atom in 4S state cannot remain uncombined for more than a few seconds and even when they combine, the amount of energy set free is too small to produce any of the characteristic reactions. We therefore conclude that production of atomic nitrogen is of course prompted by the same discharge which produces Active Nitrogen phenomenon, but the two phenomena are not connected as cause and effect.

The same remarks apply to the experiments of Broadway and Jackson¹⁵. They performed Stern and Gerlach's experiment with molecules and atoms from the discharge space and observed the splitting of the beam on a specially sensitised screen. They obtained traces which were interpreted to be due to $N\ 2p^3\ ^2P_{\frac{1}{2}}$ atoms, but this experiment only proves that such atoms are produced in the discharge space. It does not prove that the atoms persist in their free existence when we consider the afterglow space. Hence

the presence of $^2P_{\frac{1}{2}}$ atoms on the plate show that atoms are produced in the discharge and have a pretty long life, of the order of 10^{-2} second.

Thus Cario and Kaplan's theory of Active Nitrogen in which the presence of atomic nitrogen plays such a fundamental part cannot be regarded as valid unless atomic nitrogen is found in the real afterglow, quite separate from the discharge space.

Further no atomic lines of N or N^+ have so far been observed in the spectrum of the afterglow. Kichlu and Acharya⁹ failed to obtain lines of the Nitrogen atom due to transition $N\ 2p^2\ (3s-3p)$, $2p^2\ (3p-3d)$ which are at about $\lambda\ 8200$. No attempt has yet been made by anybody to obtain in the active modification the resonance lines of Nitrogen ($2p^3-2p^2\ 3s$, $2p^2\ 3d$) which are in the Schumann region below $\lambda\ 1700$. So the presence of atomic nitrogen in the afterglow has not yet been spectroscopically confirmed. The experiment would be difficult to perform for only an absorption experiment with a fluorite spectrograph can decide whether atomic nitrogen in the 4S , 2D , and 2P states is present in the afterglow, or definitely absent.

We therefore conclude that in spite of numerous experiments the presence of atomic nitrogen in any form in the active nitrogen has not yet been established.

Another point which goes against their theory is regarding the dark modification of Nitrogen which Okubo and Hamada¹⁷ have tried to attack. According to Cario and Kaplan's theory when Active Nitrogen is heated or the active gas is allowed to pass through a heated tube, the metastable molecules alone survive while the metastable atoms are destroyed. In the absence of the metastable atoms the metastable molecules will no longer be excited to the $B\ ^3\Pi$ state to emit the well-known α -bands of the afterglow. If this is so, then the total energy-content of the molecule in the "dark modification" should be much less than in the normal activated state. The best way of estimating the energy of the excited molecule is to make them collide with the vapours of such elements whose energy levels are completely known, and which do not chemically react with Active Nitrogen. Okubo and Hamada¹⁷ found that the line of highest excitation even in the case of the so-called dark modification was $\lambda\ 2654.52\ (6s6p\ ^3P-6s8d\ ^3D)$; in the case of Mercury, corresponding to the excitation energy of 9.51 volts.

Okubo and Hamada^{11,18} try to explain the enhancement of certain bands by the application of the Frank-Condon principle. The details of their paper are not available but from a short account of their work which appeared in *Physical Review* before the values of the triplet terms was known, it appears that they consider that by a discharge the Nitrogen molecule has a tendency to be excited to that particular vibration level of the B or the A state where the normal distance between the atoms (for $X\ ^3\Sigma$, $r_0=1.09$ A.U.) remains the same for the near-turning point of the

Frank-Condon diagram. Thus, there is a concentration of the atoms $A^3\Sigma^{g,11}$ as the details have not been published, it is difficult to form an accurate judgement of the value of this hypothesis.

From the foregoing short review it will appear that the existing theories of molecular structure are quite insufficient to explain the phenomenon. More well-planned experiments are needed to throw light on the subject. Lord Rayleigh's recent work proves that the surface has a strong catalytic action in accelerating the destruction of the glow. He finds that the poisoning action of the walls can be removed by treating the surface with Sulphuric Acid or Meta-phosphoric Acid. The glow then persists for $5\frac{1}{2}$ hours at least. Unfortunately, no details have yet been published regarding the spectroscopy of the segregated glow. The total intensity of the light radiated after segregation during the whole period of decay, and the absorption spectrum of the glow should be carefully measured. It has been ascertained that the decay of the glow is either bi- or tri-molecular which proves that the emission of light is provoked by collisions of two bodies or three bodies and Lord Rayleigh prefers the two-body collision. It appears to us that the phenomenon can be explained if we suppose that two excited atoms of Nitrogen N^2D or N^2P form an extremely stable state of the molecule in the following way:



The state produced is such that it does not easily transit to any of the levels A or X being forbidden by two or three selection principles. The energy of this stable state is very

nearly 9.77 volts and when this collides with a normal nitrogen molecule it gives its energy to it raising it to the B_{12} or B_{11} state or the B_0 state. These excited molecules then make the transitions according to the Frank-Condon principle giving rise to the especially enhanced bands. When the molecule collides with foreign atoms or foreign molecules it communicates its energy to the latter in exactly the same way by collision of the second type.

Attempts are being made to verify some of the suggestions.

REFERENCES

- ¹ SAHA, M. N. & SUR, N. K., *Phil. Mag.*, **48**, 421, 1924.
- ² LEWIS, E. P., *Astrophys. Jour.*, **12**, 8, 1900; *Ibid*, **20**, 49, 1904; *Phil. Mag.*, **25**, 826, 1913; *Nature*, **111**, 529, 1923.
- ³ FOWLER, A., AND STRUTT, R. J., *Proc. Roy. Soc.*, **85**, 219, 1911; **85**, 377, 1911; **86**, 56, 1911; **86**, 105, 1911; **86**, 262, 1911; **88**, 110, 1912; **92**, 438, 1916; **93**, 254, 1917.
- ⁴ MATHUR, L. S. & SENGUPTA, P. K., *Proc. U. P. Acad. Sc.*, **5**, 187, 1935.
- ⁵ BIRGE, R. T., *Nature*, **114**, 642, 1924.
- ⁶ SPONER, H., *Zeits. f. Phys.*, **34**, 622, 1925.
- ⁷ HERZBERG, G. & SPONER, H., *Zeits. f. Phys. Chem.*, **26**, 1, 1934.
- ⁸ CARIO, G. & KAPLAN, J., *Zeits. f. Phys.*, **58**, 769, 1929.
- ⁹ KICHLU, P. K. & ACHARYA, D. P., *Proc. Roy. Soc.*, **103**, 168, 1929.
- ¹⁰ OKUBO, J. & HAMADA, H., *Phil. Mag.*, **5**, 372, 1928.
- ¹¹ OKUBO, J. & HAMADA, H., *Phys. Rev.*, **42**, 795, 1932.
- ¹² KALPAN, J., *Phys. Rev.*, **45**, 675, 1934.
- ¹³ CARIO, G., *Zeits. f. Phys.*, **89**, 523, 1934.
- ¹⁴ WREDE, E., *Zeits. f. Phys.*, **54**, 53, 1929.
- ¹⁵ BROADWAY & JACKSON, *Proc. Roy. Soc.*, **127**, 678, 1930.
- ¹⁶ RAYLEIGH, LORD., *Proc. Roy. Soc.*, **151**, 572, 1935.
- ¹⁷ OKUBO, J. & HAMADA, H., *Phil. Mag.*, **15**, 103, 1933.
- ¹⁸ OKUBO, J. & HAMADA, H., *Astrophys. Jour.*, **77**, 130, 1933.

63. A NEW MODEL DEMOUNTABLE VACUUM FURNACE

M. N. SAHA AND A. N. TANDON

(*Proc. Nat. Acad. Sci. Ind.*, **6**, 212, 1936)

Received February 18, 1936.

A vacuum graphite furnace suitable for high temperature research has been described in this paper. A special feature of the apparatus is that the parts can be taken out and set again for experimental work in a very short time. Temperatures up to 2500°C can be very quickly attained within a vacuum of 10^{-4} mms. A photograph of the apparatus and four diagrams explaining its action are given.

INTRODUCTION

For some time past we have been using in this laboratory a new model vacuum furnace of which the parts are demountable. This has been found to be extremely useful

for researches on Thermal Ionisation of elements and salts and other high temperature work. With this apparatus it has been possible to attain temperatures up to 2500°C within a graphite tube very quickly. The special feature of the apparatus is that it can be taken to pieces in no time and set again for a fresh experiment. A sketch of the apparatus showing the important parts is shown in Fig. 1.

DESCRIPTION

The working of the apparatus will be clear from figures (2 and 3) which represent its horizontal and vertical

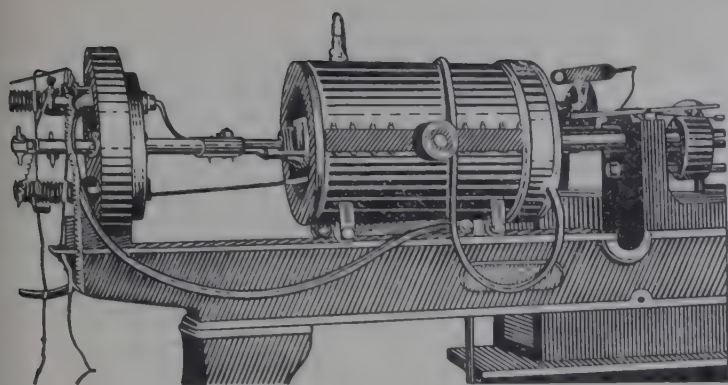


Fig. 1

sections. The main furnace consists of a water-cooled cylindrical drum C of cast iron and two hollow cast iron plates A and B which close the open ends of the drum when the furnace is working. A, B and C are all vertically mounted on a horizontal lathe bed. The plate A is fixed on one extremity of the lathe bed by the support SS as shown in figures 1 and 2. The drum C is mounted on four small wheels which enable it to slide easily over the lathe bed. The plate B is carried on the axle of a shaft which can be moved by means of a differential screw. When all internal connections and adjustments have been made, the drum C is moved to make contact with A, and B is moved by means of the differential screw and finally

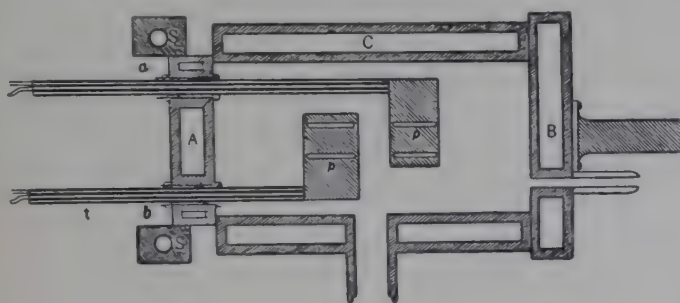


Fig. 2

tightened till the contact faces become vacuum tight. In order to ensure better contact between A and C, the support S of the plate A has been so designed that on slightly loosening the screws it itself adjusts its face in contact with that of the drum C when the vacuum is started. The apparatus is then ready for use. Although the contact faces between A, B and C are very accurately ground, in practice it is sometimes found necessary to apply a little plasticine round the edges. As all the parts A, B and C are water cooled, the contact faces remain quite cool even when the furnace is heated for hours at the highest temperature.

The fixed plate A contains four holes *a*, *b*, *c*, *d* as shown in figures 2 and 3. Through the holes *a* and *b* are inserted two water-cooled annular tubes *t* which are insulated from A by mica. The brass tubes *t* are scooped out from

solid brass rods. On the water-cooled end they carry exactly fitting heavy copper collars ending in horizontal copper plates *p* provided with slots as shown in fig. 2. Over the plates *p* are put Acheson graphite blocks G (fig. 4), to receive the furnace tube in the hollow cylindrical space. After the graphite tube is put in position, the upper

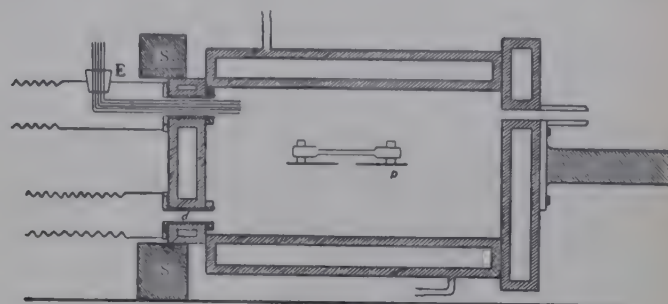


Fig. 3

part of the graphite blocks G are put over it, and the tube is then tightened by means of iron bolts. It is very important that the graphite tube should exactly fit in the blocks. The slightest loose contact between the tube and the graphite blocks causes arcing and makes the temperature of the furnace unsteady. For this reason it becomes necessary sometimes to insert some thin copper foils round the ends of the Acheson graphite tube before putting it between the graphite blocks.

The manner in which the electrodes are attached to the plate A becomes clear from fig. 5, which shows an enlarged drawing of this coupling. A brass tube having threads on one end and a collar K on the other is carefully soldered to the scooped out rod *t* at the desired distance. Over this is wrapped some mica *m* and is then put inside the hole *a* of the plate A. The collar is also insulated from the plate A by mica washers *m*. In order to make perfect vacuum-tight coupling a rubber washer R is put on the other side and the electrode is fixed in position by tightening the nut N. This arrangement is specially advantageous for two reasons, firstly that the electrodes can be taken out whenever required; secondly, the thick copper plates *p* which are attached to the electrodes can be brought out to the same level by slight adjustments of the nuts N. This precaution is particularly necessary for the fact that if the electrode plates are not in the same level, the furnace tube which is put on them by means of the graphite plugs G, as described above, encounters a mechanical strain which very often breaks it.

Through the holes *c* and *d*, each 2.5 cms. in diameter are connected two four-stage mercury pumps. For our climate (Allahabad) we have found it useful to increase the length of the cast-iron tube which is placed over the conical mouthpiece of the pump. This can be cooled by a freezing mixture. The connection is taken by means of a side tube on the top. The connecting pieces between the

pumps and the holes *c* and *d* are Tombac tubings provided with brass end pieces. The coupling between the Tombac tubing and the plate A is done in the same way as that of the electrodes and the vacuum tight contact is obtained by rubber washers. On the pump side the Tombac tube is connected by carefully ground brass cones. With such arrangement the pumps are very quick acting and even with one pump a vacuum of 10^{-4} mms is reached within a short time after starting the pump.

The brass piece of one of the Tombac tubings is bigger in length and has a hole through which passes an ebonite block E (fig. 3) which can carry all the electrical connections inside the furnace.

The water-cooled sliding drum C contains a side-tube through which the inside of the furnace can be inspected.

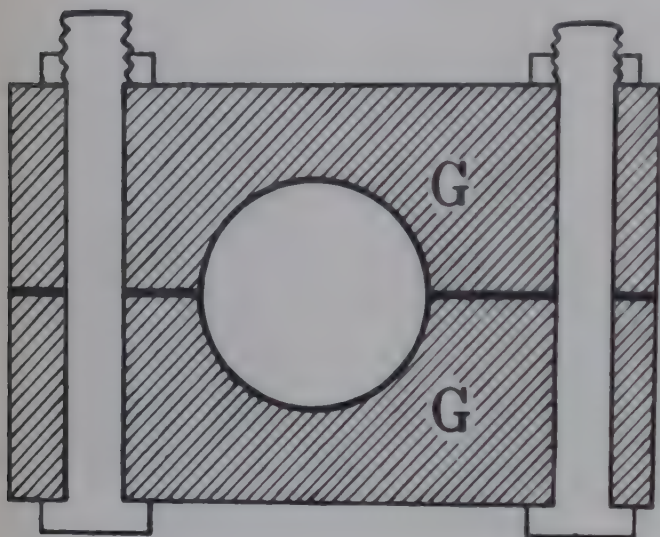


Fig. 4

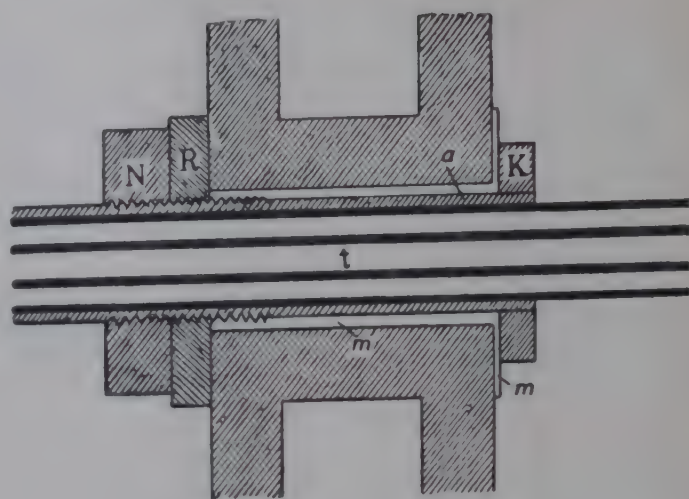


Fig. 5

This also enables the temperature of the furnace to be measured from outside by means of a disappearing-filament type of pyrometer. A thermo-couple can be inserted through this hole whenever required.

The movable plate B has a single hole through which a discharge tube can be inserted for giving an indication of the degree of vacuum.

The electrodes are connected by thick copper leads to a low-tension transformer (capacity 12 K. W.). A current of the order of 1000 amperes is allowed to flow through the graphite tube to raise it to a high temperature. The transformer has got four other ranges for giving less temperature.

We wish to express our sincere indebtedness to the Royal Society of London for giving us a grant of £150 which has enabled us to construct the furnace and to buy its accessories. Our thanks are also due to Messrs Allahabad Foundry for the casting of the plates and the water-cooled drum.

64. A STRATOSPHERE SOLAR OBSERVATORY

(*Harvard College Observatory Bulletin*, 905, 1937)

It is well known that our observations on the spectra of the Sun and the stars are limited to the redward side of $\lambda 2900$, the ultraviolet part being absorbed in the upper atmosphere, at a height of between twenty and fifty kilometers, by a layer of ozone (equivalent to 3 mm. of gas at N.T.P.) now known to arise from the photochemical action of the ultraviolet rays of the Sun on oxygen molecules. This amount of ozone, tiny as it is, is sufficient however to cut off the spectrum between $\lambda 2900$ and 2200 almost completely, though absorption begins to be perceptible from $\lambda 3200$. Below $\lambda 2060$, the extinction of the spectrum

is due to absorption by molecular oxygen and nitrogen. According to some investigators, there is a so-called window between $\lambda 2300$ and 2100 , but evidence on this point is divergent.

The abrupt termination of solar and stellar spectra below $\lambda 2900$ has been a great handicap to the advancement of our knowledge of the heavenly bodies, because the information gained from study of the spectrum beyond $\lambda 2900$ is not sufficient to explain the problems of stellar mechanisms operative there. To take one example: the great intensity of the Balmer series and the associated

continuous spectrum in the chromosphere has given rise to a large number of speculative theories which have again and again been obliged to fall back upon certain plausible hypotheses regarding the strength of the Lyman lines. If these lines could have been observed, the problem of hydrogen excitation in the Sun and stars would probably have received complete elucidation, and the problems of stellar atmospheres would have been nearer solution.

It is therefore not surprising that when some years ago Cario (Nature, **122**, 810, 1928) made the suggestion that the North Polar region, being free from illumination by the Sun during the winter, might not contain any ozone, and therefore observations carried out there might extend stellar spectra much further on the violet side of $\lambda 2900$, the suggestion was greatly welcomed. It was a disappointment for the astronomical world when observations by Rosseland (Nature, **123**, 207, 761, 1929) did not confirm Cario's hypothesis. The reason for this failure is now well understood, for Dobson and Götz [Proc. Roy. Soc., Ser. A, **122** (1929) and **129** (1930)], in their survey of the ozone content of the atmosphere at different latitudes, have shown that the amount of ozone in the atmosphere fluctuates with the season, rising at Abisko (latitude 68°N) from 2.40 mm in the middle of September to 3.6 mm in the middle of March. There is thus actually an increase in the ozone content during winter. This fact, apparently at variance with the theory of the photochemical origin of O_3 , has been satisfactorily explained by S. Chapman (Mem. Roy. Met. Soc., **3**, No. 26, 1930). The explanation is roughly as follows: The solar rays not only form ozone, but also destroy ozone. Every quantum of light between $\lambda 1750$ and 2060 produces, on being absorbed, two molecules of O_3 out of atmospheric oxygen. But this ozone absorbs strongly the light between $\lambda 2300$ and 3000 , and every quantum absorbed converts two O_3 molecules into three O_2 molecules after a number of subsidiary reactions. The actual number of ozone molecules existing at any time depends upon the equilibrium between these two groups of opposing reactions. It appears that during a polar winter, when sunlight no longer illuminates the upper atmosphere, the ozone molecules already formed continue to exist, the destructive agency having been withdrawn. One always incurs a risk in extrapolating, but, as far as evidence goes, it appears certain that during winter the atmosphere of regions a few degrees removed from the North Pole also retains its ozone screen, so that observations of stellar spectra (the Sun does not come into view, as it is below the horizon) will have no chance of taking us beyond the limit attainable in more hospitable climates.

Regener's Work.—The recent discovery by Götz, Meetham, and Dobson (Proc. Roy. Soc., A **145**, 416, 1934) that the ozone screen does not lie between fifty and one hundred kilometers as was formerly thought, but is confined between twenty and forty kilometers, affords a

definite opportunity of extending stellar spectra beyond $\lambda 2900$, as has actually been demonstrated by E. and V. Regener (Phys. Zeits., **35**, 788, 1935). Professor Regener has developed a fine technique of sending into the upper atmosphere balloons carrying automatic recording apparatus for measurement of the intensity of cosmic rays. His highest record has been thirty-one kilometers where, according to the estimates of Dobson and Götz and confirmed independently by the Regeners, two-thirds of the total ozone remains below. In the course of his last reported work in 1934, he sent along with his cosmic ray apparatus a quartz-spectrograph provided with automatic shutters and pointed toward a matt surface below, which was illuminated by sunlight. The time of exposure was short, and the reflecting power of the matt surface for the ultraviolet rather feeble. In spite of these disadvantages they were able to show that with increasing altitude the spectrum extended further into the ultraviolet, and that at the greatest height reached by their apparatus the limit was extended by about a hundred units beyond the limit reached by the same apparatus for the same exposure on the ground. If the exposures had been longer, and the surface had had a better reflecting power for $\lambda 2800$, it is clear that the spectrum might have extended much further than the lowest limit attained so far. They also confirmed the finding of Dobson and Götz that most of the ozone is to be found between twenty and thirty-five kilometers, that above forty kilometers the total amount is one-twelfth of the whole, and that above fifty kilometers it is barely two per cent of the whole.

The pioneering work of Regener has shown the practical possibility of having a "Stratosphere Solar Observatory". It can now be confidently expected that if a regular program can be organized for sending balloons to a height of thirty-five to forty kilometers, provided with quartz, fluorite, and vacuum spectrographs of sufficient light-gathering power, our knowledge of the solar spectrum beyond $\lambda 2900$ will receive a great impetus. The Russian worker Moltchanoff claims that he has reached a height of forty kilometers with a balloon provided with Radio-Sonde signalling apparatus; it is therefore to be hoped that within the near future the problem of photographing the solar spectrum at a height of forty kilometers will be definitely solved.

Let us consider in some detail the practical possibility of such a program, and the extension of the solar spectrum that can be expected. The absorption coefficient of ozone (Ladenberg, Journ. Opt. Soc. Am., **25**, No. 9, 1935) can be expressed by Beer's Law

$$D = \frac{I}{I_0} = e^{-a'l} = 10^{-a'l'}$$

The values of a' are given in the accompanying table

taken from Ladenberg's paper (*op. cit.*), together with the computed values of a .

	$\lambda=2300$	2400	2500	2600	2700	2800	2900
a'	50	95	120	120	100	48	15.5
a	115	219	278	278	230	111	35.8

The path length of ozone at (N.T.P.) necessary to reduce the rays to one-half of their original intensity, say for $\lambda\lambda 2500-2600$, is found from the relation

$$D = \frac{1}{2} = e^{-278I},$$

$$\text{or } I = \frac{\log_e 2}{278} = 2.4 \times 10^{-3} \text{ cm.}$$

A glance at the figures given by Götz and Dobson shows that at Arosa the amounts of ozone lying above the observer at different heights are (according to method B; total amount = 0.300 cm):

Height in km	4.9	13.1	20.6	28.1	35.9	45.1
Ozone in cm	0.263	0.186	0.1279	0.0389	0.0045	0

Thus at 36 km, the rays $\lambda\lambda 2500-2600$ will be reduced in intensity to about one quarter, while the rays on either side will be less absorbed. At a height of forty kilometers, recently announced to have been reached by a Soviet balloon carrying Radio-Sonde apparatus, the solar spectrum should be transmitted in practically undiminished intensity over most of the range from $\lambda\lambda 2900$ to 2300.

How Much Can Be Observed of Wave-lengths below $\lambda 2300$?—We may now discuss the question of absorption due to other constituents of the atmosphere. At these heights only O_2 and N_2 need be considered.

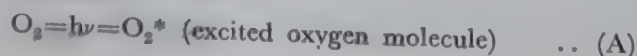
1. OXYGEN. It has been shown elsewhere (M. N. Saha, On the Action of Ultraviolet Solar Rays on the Upper Atmosphere, communicated to the Proc. Roy. Soc. London) that on certain plausible assumptions it is possible for us to calculate the amount of O_2 gas lying above two kilometers, in terms of a column at N.T.P. (1 cm at N.T.P. = 2.79×10^{19} molecules). The figures are quoted below:

Height in km	30	40	50	60	100
O_2 in cm	1200	200	7	0.60	0.044

Now from laboratory experiments we know that oxygen shows the following absorptions:

(a) A feeble set of bands at $\lambda\lambda 2429-2595$, which probably correspond to the dissociation of O_2 into O^3P , O^3P (Herzberg). This absorption is very feeble. Even a twenty five meter column of O_2 gas at N.T.P. shows hardly any absorption. Hence the superincumbent layer of O_2 above 30 km will transmit all rays between $\lambda\lambda 2400$ and 2900.

(b) The Runge-Schumann absorption bands. These bands extend from $\lambda\lambda 2060$ to 1700 and produce the following photochemical effect:



Hence it is certain that a solar spectrum taken at a height of 36 km will not show the region between $\lambda\lambda 1750$ and 1300.

At $\lambda 1750$ the band absorption passes into continuous absorption, extending to $\lambda 1250$ and giving rise to the photochemical dissociation of oxygen into a normal and an excited atom as follows:



Both these reactions, particularly (A), give rise to ozone. It has been shown elsewhere that the rays $\lambda\lambda 2060-1750$ are absorbed in the ozone layer between 35 and 20 km and give rise to ozone. Hence when we are making observations above 35 km, the region $\lambda\lambda 2060-1750$ is expected to come out strongly on the plates. This in itself will give us information about our atmosphere which is bound to be of great importance to meteorologists.

The continuous absorption at $\lambda\lambda 1750-1250$ is much stronger and rises to a maximum at $\lambda 1460$. At this wave-length, 1/500 cm of O_2 at N.T.P. according to Ladenberg reduces the light to half its intensity. As shown above, the absorption will be completed between 100 km and 200 km; this is in accordance with the Cabannes' observation (see report on the luminous night sky by Dejardin, Rev. Modern Phys., Jan. 1936) that the red auroral lines $O^3P-O^1D_2$, $\lambda\lambda 6363$ and 6300, originate from above a height of 200 km.

(c) Oxygen is found to have rather feeble absorption between $\lambda\lambda 1250-1100$. In fact, Lyman showed that these wave-lengths can easily pass through three to four centimeters of O_2 and N_2 at N.T.P. A glance at the above tabulation shows that at a height of fifty kilometers we can expect transmission of the region $\lambda\lambda 1250-1100$.

2. ABSORPTION BY NITROGEN.—The amounts of nitrogen over different heights are as follows:

Heights in km	20	30	40	50	60	100	200
						(E)	(F)
Amount in meters	386	94.8	20	1.10		0.11	1.4×10^{-5}

The absorption by nitrogen has been treated elsewhere, and we can only summarize the results. There is no nitrogen absorption between $\lambda\lambda 2900$ and 1700. Beyond $\lambda 1700$, the Vegard-Kaplan bands are expected to be absorbed, but it is quite possible that on account of heavy absorption by O_2 in the region, these bands may not appear.

The region $\lambda\lambda 1500-1250$ will be blocked by O_2 absorption, as already described. But even if the oxygen absorption were absent, nitrogen would have blocked this region for which it shows strong absorption bands (Birge-Sponer bands).

Transmission below $\lambda 1250$.—On account of paucity of laboratory experiments below $\lambda 1250$ regarding absorption by O_2 and N_2 , we can speak with much less confidence. Price and Collins (Phys. Rev., 48, 780, 1935) obtain certain bands for O_2 between 1250 and 1000 Angstroms, which

they have not so far interpreted, at 1.5 cm of N_2 at N.T.P. It appears, therefore, that at 35 km (oxygen=200 cm), part of the solar spectrum which does not coincide with the O_2 bands may leak through. But the absorption of O_2 below 1000 to 650 is according to these authors very heavy, and nothing can be expected between these limits at 35 km. Below 650 Angstroms no prediction is possible, as laboratory data are not available, but one or two strips of continuous spectrum may be transmitted.

We conclude from the above discussion that a spectro-photogram of the sun, taken at a height of 40 km, will extend the spectrum to $\lambda 2000$, and probably no atmospheric bands will appear between $\lambda \lambda 2900$ and 2000 . Between $\lambda \lambda 2000$ and 1700 the Runge-Schumann bands of O_2 may appear in absorption. The region $\lambda \lambda 1700-1250$ will probably be completely cut off. A strip between $\lambda \lambda 1250$ and 1000 may be expected to be transmitted. Below $\lambda 1000$ no prediction can be made, as laboratory data are not available.

But access even to these limited regions will result in

invaluable additions to our knowledge, for they will afford information about the behavior of the resonance lines of most of the elements which occur in the Fraunhofer spectrum and thus ease our way for the final solution of the mysteries of solar physics; *e.g.*, we expect to get information (a) about La $\lambda 1216$ of H; (b) about $\lambda 1640$ $\left(=4 R \left(\frac{1}{2^2} - \frac{1}{3^2}\right)\right)$, $\lambda 1215$ $\left(=4 R \left(\frac{1}{2^2} - \frac{1}{4^2}\right)\right)$ of He^+ ; (c) about the existence or otherwise of the Li-continuum at about $\lambda 2300$; (d) about the resonance lines of elements from Be to O ($4 \rightarrow 8$); we shall not probably obtain any information about F and Ne, but we may obtain the Na-continuum. (e) As regards Mg, we shall obtain much desired information about the resonance lines of Mg and Mg^+ which are just beyond $\lambda 2900$; (f) the same is true of the resonance lines of the elements Al to S. (g) We hope also to obtain very valuable information regarding transitional elements, particularly Fe^+ .

The above short account will indicate how much we should gain from a "Stratosphere Observatory".

65. EXPERIMENTAL DETERMINATION OF THE ELECTRON AFFINITY OF CHLORINE

M. N. SAHA AND A. N. TANDON

(*Proc. Nat. Inst. Sci. Ind.*, **3**, 287, 1937)

(Read January 5, 1937)

It is well known that halogens have an affinity for electrons and many methods have been proposed for calculating this quantity. Let us take a halide atom X . The affinity E is given by the relation:—

$$X + e = X^- + E.$$

E can be expressed in calories, volts or wave-length units. The following table gives the values in Kilo calories obtained by different workers:—

	F	Cl	Br	I
Mayer and Helmholtz ¹ (Theoretical)	95.3	86.5	81.5	74.2
J. E. Mayer ² (Experimental)	..	..	..	72.6 $\pm$ 2
P. P. Sutton and J. E. Mayer ³ (Experimental)	..	..	..	72.4 $\pm$ 1.5
Angerer and Müller ⁴ (Spectroscopic)	94	86.6/ 89.6/	79.1/ 81.3/	71.3
E. Lederle ⁵ (Spectroscopic)	95 $\pm$ 2	90	82	73
Saha and Sharma ⁶ (Theoretical)	163.3			

There are several methods for calculating the electron affinity of the halogens. Theoretical calculations have been

made by E. Mayer and L. Helmholtz¹ from the crystal energies of the alkali halides. They used the formula for the grating energy of these salts derived by Max Born and E. Mayer². Saha and Sharma³ used an extrapolation method for calculating the electron affinities. They showed that the value of the ionisation potentials of Ne-like atoms Ne, Na^+ , Mg^{++} is given by the formula:—

$$E = (Z - 6.745)^2 + 1.917 - \frac{42.8}{(Z - 6.745)} + \frac{70.165}{(Z - 6.745)^2}.$$

If now Z is put equal to 9, we get the electron affinity for fluorine. The value so obtained is 7.1 volts; though this value is high and is rather in violent disagreement with values calculated by other workers, it is in agreement with the value calculated by Mulliken.

On the experimental side, this subject has not been much investigated and the few data that are available have been obtained indirectly from spectroscopic methods. Only in a few cases direct experimental determination has been made. An attempt was made by Angerer and Müller⁴ to calculate the electron affinity from spectroscopic

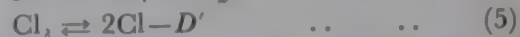
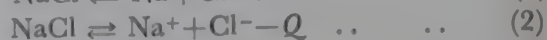
evidence. They observed the absorption spectra of the vapours of alkali halides KF, NaCl, CsCl, KBr, CsBr and KI and found that these begin to absorb continuously at high temperatures from a long wave-length limit. The continuous absorption was attributed to absorption by Cl^- or other halogen ions which was supposed to arise from thermal decomposition of the salts. The electron affinity was determined according to the quantum relation $eV = h\nu$. E. Lederle⁵ calculated the electron affinities of halogens from the data of Angerer and Müller by an application of the Born-Heisenberg method, but later on H. Kuhn⁶ showed that the calculation was based upon a wrong interpretation of the experimental results. Attempts have also been made to observe the emission spectra due to the capture of electrons by neutral halogen atoms, but so far nothing indicative of the actual occurrence of such a process has been observed. Oldenberg⁷ tried to observe the electron-affinity spectrum with improved experimental technique, but failed to observe any new spectrum. He gave a theoretical explanation of his negative result. It amounted to showing that the probability of capture of electrons by neutral halogen atoms is very small compared to that of capture of electrons by positive ions like Na^+ leading to the formation of neutral atoms.

At the suggestion of Born and Franck, a direct method was used by J. E. Mayer⁸ to determine experimentally the electron affinity of iodine. He studied the thermal ionisation of the iodides of caesium and potassium at temperatures of the order of 1160°K . and calculated the equilibrium constant; from this, by an application of the dissociation formula and thermochemical data, he could calculate the electron affinity. Recently P. P. Sutton and J. E. Mayer⁹ have described another general method for the determination of electron affinity and applied it to determine that of iodine. In Mayer and Sutton's method a tungsten filament was heated in an evacuated globe in which iodine vapour could be introduced. The iodine vapour molecules on coming into contact with the strongly heated filament suffer dissociation into atoms, some of which attract electrons and become negatively charged. These negatively charged atoms and electrons are collected by a concentric anode cylinder. By means of a magnetic field, the electrons are switched off and the current due to the negatively charged iodine atoms can be measured. The value obtained for the electron affinity of iodine was found to be 72.4 ± 1.5 Kilo cal. But so far no direct experimental determination on these lines of the electron affinity of the other halogens has been carried out.

The method described in this paper is also of very general application and is based on the study of the thermal ionisation of alkali halide vapours at high temperatures. The principle involved is of the same nature as that used by J. E. Mayer⁸, but the experimental technique has been much improved and is altogether different.

The method essentially consists in vaporising the alkali halide in an electric furnace and then bringing it to a region of higher temperature where the vapour molecules suffer thermal dissociation into atoms as well as into ions. The products of dissociation are made to pass through a narrow circular opening, and then through a circular diaphragm into a Faraday cylinder where they are collected and the current measured by a galvanometer.

The process of dissociation inside the high temperature region, where free electrons are also present, is given by the following set of equations. Taking sodium chloride as a typical example the possible processes of dissociation can be written as follows:—



where D is the heat of dissociation of NaCl, Q the heat of dissociation into a sodium and a chlorine ion, I the ionisation potential of sodium and E the electron affinity of chlorine. D' is the heat of dissociation of chlorine into atoms. The dissociation of diatomic molecules has been studied in detail and the formula has been worked out by Gibson and Heitler¹⁰ (see also *Treatise on Heat*, by Saha and Srivastava, p. 703, 1935) with the aid of quantum mechanics. They have taken into account the translational, rotational and vibrational states of the molecules and also the effect of nuclear spin, and given the expression for the entropy and other thermodynamical functions of diatomic molecules. If ψ be the thermodynamical potential given by the relation

$$\psi = S - \frac{U + pV}{T},$$

where U is the internal energy, S the entropy, T the absolute temperature, p the pressure and V the volume, then the expression for ψ is given by

$$\psi = -\frac{U_0}{RT} + \frac{7}{2} \ln T - \ln p + \ln \left[\frac{(2\pi m)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \frac{8\pi^2 I k}{h^2} \left\{ \frac{3}{2} + \frac{1}{2} \right\} \right] - \ln \left(1 - e^{-h\nu/kT} \right) + \ln g_n$$

according as the nuclei have got a spin or not. m is the mass of the molecule, I its moment of inertia and g is the weight factor.

Hence, we have

$$\begin{aligned} \psi_{\text{NaCl}} &= -\frac{U_{0\text{NaCl}}}{RT} + \frac{7}{2} \ln T - \ln p_{\text{NaCl}} - \ln \left(1 - e^{-h\nu/kT} \right) \\ &\quad + \ln \left[\frac{(2\pi m_{\text{NaCl}})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \frac{8\pi^2 I k}{h^2} \right] + \ln g_{\text{NaCl}} \\ \psi_{\text{Na}} &= -\frac{U_{0\text{Na}}}{RT} + \frac{5}{2} \ln T - \ln p_{\text{Na}} + \ln \frac{(2\pi m_{\text{Na}})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} + \ln g_{\text{Na}} \\ \psi_{\text{Cl}} &= -\frac{U_{0\text{Cl}}}{RT} + \frac{5}{2} \ln T - \ln p_{\text{Cl}} + \ln \frac{(2\pi m_{\text{Cl}})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} + \ln g_{\text{Cl}} \end{aligned}$$

$$\text{Hence } \ln \frac{p_{\text{Na}} p_{\text{Cl}}}{p_{\text{NaCl}}} = -\frac{D}{RT} + \frac{3}{2} \ln T + \ln \left(1 - e^{-hv/kT}\right) + \ln \frac{g_{\text{Na}} g_{\text{Cl}}}{g_{\text{NaCl}}} - \ln \left[\frac{k^{\frac{3}{2}}}{2^{\frac{3}{2}} \pi^{\frac{1}{2}} I h} \left(\frac{m_{\text{NaCl}}}{m_{\text{Na}} m_{\text{Cl}}} \right)^{\frac{3}{2}} \right].$$

Since $\psi_{\text{NaCl}} = \psi_{\text{Na}} + \psi_{\text{Cl}}$.

In this case $g_{\text{Na}} = 2$, $g_{\text{Cl}} = 4$, $g_{\text{NaCl}} = 1$ therefore, we have

$$\ln k_1 = \ln \frac{p_{\text{Na}} p_{\text{Cl}}}{p_{\text{NaCl}}} = -\frac{D}{RT} + \frac{3}{2} \ln T + \ln \left(1 - e^{-hv/kT}\right) + \ln \left[\frac{2^{\frac{3}{2}} k^{\frac{3}{2}}}{\pi^{\frac{1}{2}} I h} \left(\frac{m_{\text{NaCl}}}{m_{\text{Na}} m_{\text{Cl}}} \right)^{\frac{3}{2}} \right].$$

Similarly we have

$$\ln k_2 = \ln \frac{p_{\text{Na}} p_{\text{Cl}}}{p_{\text{NaCl}}} = -\frac{Q}{RT} + \frac{3}{2} \ln T + \ln \left(1 - e^{-hv/kT}\right) + \ln \left[\frac{k^{\frac{3}{2}}}{2^{\frac{3}{2}} \pi^{\frac{1}{2}} I h} \left(\frac{m_{\text{NaCl}}}{m_{\text{Na}} m_{\text{Cl}}} \right)^{\frac{3}{2}} \right].$$

Since $g_{\text{Na}^+} = 1$, $g_{\text{Cl}^-} = 1$,

$$\ln k_3 = \ln \frac{p_{\text{Na}} p_e}{p_{\text{Na}}} = -\frac{I_0}{RT} + \frac{5}{2} \ln T + \frac{(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3}$$

$$\ln k_4 = \ln \frac{p_{\text{Cl}} p_e}{p_{\text{Cl}^-}} = -\frac{E}{RT} + \frac{5}{2} \ln T + \ln \left[\frac{(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3} \right] + \ln 8.$$

It is easy to verify that these constants are not independent, but we have

$$k_4 = \frac{k_1 k_3}{k_2},$$

and

$$Q = D + I - E.$$

k_2 is determined experimentally from which we can calculate the value of Q . We obtain E from the relation

$$E = D + I - Q.$$

Apparatus.—The demountable vacuum graphite furnace used in these experiments has been described in detail in a previous paper by M. N. Saha and A. N. Tandon¹¹. It will suffice here only to mention the internal connections inside the furnace. These are illustrated in the adjoining diagram (Fig. 1). The high temperature is produced in the graphite tube F which is heated by passing a current of about a thousand amperes from a low tension transformer. The graphite tube has only a small hole A on one side and female cone C on the other. Into the female cone is inserted another wire-wound furnace whose male cone exactly fits C , so that the salt vapour can only pass through the hole A . The wire-wound furnace F' is so designed that the temperature of the salt vapour can be determined without much error, and the salt vapour does not condense in any part between this and the graphite tube. An iron rod is bored from both the ends and a very thin iron partition is left. One end of this tube is then made conical so as to fit exactly into the cone of the graphite tube. The tube is then bent into the shape as shown in figure (1), so that the molten salt may not run down

the graphite tube. The thermocouple T is placed on the other side of the diaphragm as shown in the figure. Over the iron tube some mica is put and then the furnace is made by winding nichrome wire on it. The cone C is pushed inside the graphite tube, into a temperature region which is greater than the temperature at which the salt vaporises. This ensures that the salt vapour does not condense between the furnace and the high temperature region.

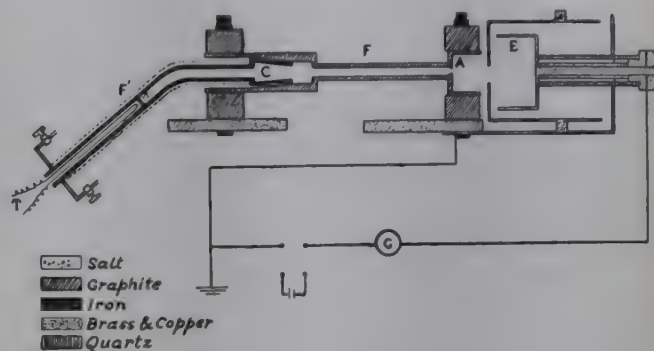


Fig. 1

The salt to be investigated is put inside this furnace and the temperature is measured by means of a thermocouple.

At a distance d from the small hole in the graphite is put a diaphragm D of radius r , behind which is placed a Faraday cylinder E . The cylinder is connected to a sensitive galvanometer. If S denotes the area of the circular orifice, the number of particles coming out of the hole per second is given by $\frac{S}{4} n \bar{c}$, where n is the number of particles per cubic centimeter inside the graphite tube and $\bar{c}$ the mean velocity at the temperature of the graphite tube.

Now the pressure $p = nkT$ or $n = p/kT$ where p is the pressure of the particles inside the tube.

If p_M^+ be the partial pressure of the positive ions inside the tube, then the number of positive particles coming out per second is equal to $\frac{S}{4} \frac{p}{kT} \bar{c}$ and therefore the positive ion current i_M^+ is given by

$$i_M^+ = \frac{S}{4} \frac{p_M^+}{kT} e \sqrt{\frac{8kT}{m\pi}}.$$

If i_θ is the current indicated by the galvanometer

$$i_M^+ = \frac{2d^2}{r^2} i_\theta,$$

therefore

$$p_M^+ = \frac{i_M^+}{eS} \sqrt{2\pi m_M kT}.$$

Similarly

$$p_X^- = \frac{i_X^-}{eS} \sqrt{2\pi m_X kT}.$$

If p_{MX} denotes the vapour pressure of the salt MX , then

the dissociation constant K_2 is equal to $\frac{p_{M^+} \cdot p_{X^-}}{p_{MX}}$ and is therefore given by the expression

$$K_2 = \frac{i_{M^+} i_{X^-}}{e^2 S^2} (2\pi k T) \sqrt{\frac{m_M m_X}{p_{MX}}}$$

The magnitude of the currents is measured experimentally by the galvanometer. The diameter of the effusion hole is determined by means of a travelling microscope, from which S is calculated.

Experimental technique.—It is first of all necessary to study the emissions from the graphite tube when no salt is put inside the subsidiary furnace. For this reason the furnace tube is heated for an hour at a temperature of about 2000°C. in a vacuum of about 10^{-4} mms. The process is continued till the vacuum remains undisturbed by the heating of the graphite tube.

The Faraday cylinder is then given a small positive or negative voltage with respect to the graphite tube from a potential divider and the current due to electrons and positive ions is measured at different temperatures with different applied voltages. The positive current is found to be negligible in comparison to the negative current, which must be due to electrons emitted from the graphite tube.

The furnace is then opened and the salt is introduced into the subsidiary furnace. After proper degassing of the graphite tube the current in the subsidiary furnace is switched on. The temperature takes a steady value in about 15 minutes. The currents due to the positive and negative ions is measured again in the manner described above by giving the Faraday cylinder a small negative or positive potential with respect to the graphite tube, which is always kept at earth potential. The retarding potential is usually kept two volts but in the case of lithium chloride, the order of the electron current is comparable with the current due to the chlorine ions and so while measuring the chlorine ion current the retarding potential is kept very low. If the potential is kept high the electrons are accelerated and an unusually high current is recorded.

The temperature of the graphite tube is recorded by means of a disappearing filament type of pyrometer having two ranges. A nickel nichrome thermocouple is used to indicate the temperature at which the salt vaporises. It is very necessary that during the experiment the temperatures remain steady. There is no difficulty in maintaining steadiness of temperature in the case of the subsidiary furnace, but the temperature of the graphite tube sometimes fluctuates by small amounts due to the fluctuations in the voltage of the supply mains. For this reason, it becomes necessary to record the temperature of the graphite tube at very short intervals.

The experiments have been performed with three salts, KCl, NaCl and LiCl. The results obtained with each salt are given below and discussed separately.

Potassium Chloride

The heat of ionisation of potassium is well known to be 99.5 Kilo calories. The heat of dissociation of potassium chloride into a potassium and chlorine atom is known to be 101.4 Kcal. The order of ion currents obtained in this case is of much greater order than the electron current (obtained from a blank experiment) and therefore the presence of the latter does not disturb the equilibrium represented by equation (2). Theoretically the positive ion current and the current due to chlorine ions should vary inversely as the square root of their atomic weights, and the effect of the extra electrons due to the graphite should increase the proportion of chlorine ions, but on the contrary it was found in many cases that the positive ion current was slightly larger than the chlorine ion current at low temperatures. This is probably due to the formation of molecular chlorine, according to equation (5), which diminishes the pressure of chlorine atoms, and hence the chlorine ion concentration decreases according to the equation (4). At higher temperatures the formation of molecular chlorine diminishes and more electrons are given out by the graphite tube, hence the current due to the chlorine ions increases in proportion. Table 1 gives the results of observations. The vapour pressure of KCl was directly extrapolated from the empirical formula of Fiösch and Rodebush.¹²

$$\log p_{mm} = \frac{9115}{T} + 8.3526.$$

TABLE 1

Diameter of the effusion hole (mms.)	Vapour pressure (dynes/cm ²)	Temperature of the graphite tube (°C)	$i_{K^+} \times 10^6$ (amps.)	$i_{Cl^-} \times 10^6$ (amps.)	$K \times 10^5$	Q (Kilo cals.)
1.17	90.95	1620	583.4	583.4	127.6	114.7
"	84.48	1560	37.04	34.61	52.72	114
"	27.66	1530	24.5	21.78	41.6	113.6
"	15.2	1380	4.668	4.279	3.909	111
4.955	28.3	1625	11.97	17.96	114	114.8
"	15.55	1625	16.16	15.19	276.2	112
"	17.33	1550	8.079	5.171	40.51	114.2
"	111.1	1540	25.22	12.93	49.03	112.9
"	17.33	1520	5.819	3.555	19.72	114.8

Taking the mean of the above values of Q we get 113.5 Kilo calories, and hence from the formula $E = D + I - Q$ we get $\{99.5 + 101.4 - 113.5\} = 87.4$ Kilo calories for the value of the electron affinity of chlorine.

Sodium Chloride

The results obtained with sodium chloride vapour are given in table 2. It will be found that the positive ion current is much larger than the current due to the negatively

charged chlorine ions, specially at low temperatures and pressures. The atomic weight of sodium (23) is smaller than that of chlorine (35.5) and so the effusion current due to Na^+ should be larger by 1.243 times, but it will be seen that the current is sometimes twice or even more. The cause is again due to the formation of molecular chlorine as explained in the case of potassium chloride. At high temperatures the proportion of chlorine ions increases. The vapour pressure of sodium chloride has been calculated from the empirical formula of Fiösch and Rodebush¹².

$$\log_{10} p_{mm} = -\frac{9419}{T} + 8.3297.$$

TABLE 2

Diameter of the effusion hole	Vapour pressure (dynes/cm ²)	Temperature of the graphite tube (°C)	$i_{\text{Na}^+} \times 10^7$ (amps.)	$i_{\text{Cl}^-} \times 10^7$ (amps.)	$K \times 10^7$	Q (Kilo cal.)
1.17 mm.	82.59	1625	70.37	57.57	128.5	132.4
"	11.71	1620	27.52	25.6	180.3	131.7
"	61.37	1600	103.7	64.82	283.2	127.7
"	41.49	1560	74.54	45.37	206.3	126
"	15.81	1505	21.34	5.762	19	130.5
"	11.71	1500	14.41	5.403	16.26	130.7
"	76.9	1470	30.4	14.99	14.24	128.7
"	15.81	1450	11.89	3.60	6.439	130
"	11.71	1450	7.565	2.881	4.422	131.3
"	31.11	1440	10.87	4.478	3.701	131.1
"	76.9	1400	21.07	9.317	5.895	126.3

The average of Q from the above comes out to be 129.7 Kilo calories. The heat of dissociation of sodium chloride into sodium and chlorine is known to be 97.7 Kilo calories and the ionisation potential of sodium is 117.9 Kilo calories. The electron affinity of chlorine is therefore $(97.7 + 117.9 - 129.7) = 85.9$ Kilo calories.

Lithium Chloride

It has been seen in the ionisation of KCl and NaCl that the current due to chlorine ions is diminished due to the formation of molecular chlorine. It is therefore to be expected that in the case of lithium chloride the proportion of chlorine ions would be much smaller. On the contrary it was found that the number of chlorine ions was much larger than the number of lithium ions. Lithium has a high ionisation potential of 123.8 Kilo calories and the heat of dissociation of LiCl is also very large (114.4 Kilo calories). The order of currents obtained at the temperatures used (1400°C.—1625) is therefore of much smaller magnitudes than the corresponding currents for KCl and NaCl. The electron current due to the emission from the graphite tube was negligible in the latter cases, but in this case it is of the same order as the current due to the ions.

The effect of a large percentage of free electrons will naturally be to retard the ionisation of lithium and to accelerate the formation of chlorine ions. It is for this reason that chlorine ions are present in such a large proportion.

As no arrangement has yet been made to distinguish between the negative ion and electron currents, it has been supposed here the negative current is all due to the chlorine ions. This may introduce an error in this case. Attempt was made to carry out the experiments at low temperatures in the absence of free electrons but then the currents were so small that the galvanometer could not detect them. One extra precaution has however been taken in this case. The retarding potential, while measuring the chlorine ion current, was kept very low (0.5 volt) because of the presence of electrons. A large voltage accelerates the electrons and an unusually high current is obtained.

The results obtained are tabulated in table 3. The vapour pressure has been extrapolated from the formula given by Wartenburg and Schulz¹³

$$\log p_{atm} = -\frac{37200}{4.57T} + 4.923.$$

TABLE 3

Diameter of the effusion hole	Vapour pressure (dynes/cm ²)	Temperature of the graphite tube (°C)	$i_{\text{Li}^+} \times 10^8$ (amps.)	$i_{\text{Cl}^-} \times 10^8$ (amps.)	$K \times 10^{10}$	Q (Kilo cal.)
1.17 mm.	139	1660	98.54	262.8	2743	148.7
"	360.6	1640	102.2	240.8	979.7	151.1
"	139	1625	73	175.2	1330	148.8
"	203.7	1620	43.8	153.3	475.2	152.4
"	77.27	1610	37.35	79.41	550.9	150.9
"	77.27	1575	32.79	42.05	250.4	150.9
"	307.6	1420	9.344	9.344	3.659	152

CONCLUSION

In this paper is described an experimental method for finding out the electron affinity of the halogens. The method has for the present been applied to chlorine only. The value of this quantity, from the two sets of most reliable determinations, comes out to be 86.6 Kilo cals, and the theoretical value given by Born, Mayer and Helmholtz¹ is also 86.5. The results are therefore in perfect agreement with the theory. Further experiments are in progress for finding out, according to this method, the electron affinity of the other halogens.

We wish to record our sincere thanks to the Royal Society of London for the award of a grant which enabled us to construct the vacuum furnace, and buy the pyrometer, thermocouples, and other apparatus mentioned in the paper.

REFERENCES

- ¹ E. MAYER and L. HELMHOLTZ,—*Zeits. f. Phys.*, vol. **75**, p. 19, (1932).
- ² MAX BORN and E. MAYER,—*Zeits. f. Phys.*, vol. **75**, p. 1, (1932).
- ³ M. N. SAHA and R. SHARMA,—*Bull. Acad. Sc. U.P.*, vol. **1**, p. 119, (1931-32).
- ⁴ ANGERER and MÜLLER,—*Phys. Zeits.*, vol. **26**, p. 643, (1925).
- ⁵ E. LEDERLE,—*Zeits. f. Phys. Chem. B.*, vol. **17**, pp. 84, 85, 353, (1932).
- ⁶ H. KUHN,—*Zeits. f. Phys. Chem.*, vol. **19**, p. 227, (1932).
- ⁷ Oldenberg,—*Phys. Rev.*, vol. **43**, p. 534, (1933).
- ⁸ J. E. MAYER,—*Zeits. f. Phys.*, vol. **61**, p. 798, (1930).
- ⁹ P. P. SUTTON and J. E. MAYER,—*Jour. Chem. Phys.*, vol. **3**, p. 20, (1935).
- ¹⁰ GIBSON and HEITLER,—*Zeits. f. Phys.*, vol. **49**, p. 465, (1928).
- ¹¹ M. N. SAHA and A. N. TANDON,—*Proc. Nat. Acad. Sc. India*, vol. **6**, p. 212, (1936).
- ¹² FIOCH and RODEBUSH,—*Jour. Am. Chem. Soc.*, vol. **48**, p. 2552, (1926).
- ¹³ WARTENBURG and SCHULZ,—*Zeits. f. Elec. Chem.*, vol. **27**, p. 568, (1921).
- ¹⁴ M. N. SAHA and B. N. SRIVASTAVA, *A Treatise on Heat*, p. 703.

66. MOLECULES IN INTERSTELLAR SPACE ?

(Nature, **139**, 840, 1937)

In a recent note in NATURE¹, and more in detail elsewhere,² Dr. T. Dunham, jun., has described his discovery of more interstellar lines due to K ($\lambda 7699.03$), Ca ($\lambda 4227$), Ti⁺ ($\lambda 3242.6$ and others) and a number of other lines the origin of which has not yet been traced ($\lambda 3957.7$, $\lambda 4300.3$, $\lambda 4232.6$). We have to add to these Merrill's interstellar lines³ ($\lambda 5780$, $\lambda 6284$).

Dunham's work and his discussion of the occurrence of Ti⁺-lines forms a landmark in the story of interstellar investigations, as it throws clear light on the mechanism of excitation, and removes a good deal of misconception arising out of the former idea that only Ca⁺-lines, and the sodium D-lines occur in interstellar space.

Dunham's discovery that only such Ti⁺-lines which arise from absorption in the lowest orbit of Ti⁺ ($3d^2$, $4s$, $^4F_{3/2}$) occur as interstellar lines and that no Ti⁺ atom in the next excited state Ti⁺ ($3d^2$, $4s$, $^4F_{5/2}$ excitation potential 0.012 volt) occur in interstellar space, shows that the reaction between matter and radiation in interstellar space is of a kind which cannot be described in terms of any interspace temperature. The temperature in interspace is very nearly absolute zero, and ionization is produced only by the photochemical action of quanta meeting atoms or ions after long intervals of time in space. The recombination between ions and electrons also take place at very long intervals. The result is that only such states of atoms and ions occur in interstellar space as have infinitely long life.

The argument raises the question: Why should not molecules also occur in interstellar space? In fact, the

above arguments, if forced to their logical conclusion, lead us to the view that we should have molecules in interstellar space. Merrill in fact notes that the lines $\lambda 5780.4$, and $\lambda 6284.0$ discovered by him are diffuse, and in course of a conversation told me that they might be molecular in origin. In fact, the line $\lambda 6283.0$ appears decidedly to be due to molecular sodium, Na₂, due to the transition (Na₂: $^2S^3S A \ ^1\Sigma \rightarrow \ ^2S. \ ^2P B \ ^1\Sigma, n''=0, n'=8$). This band is obtained in absorption in molecular sodium, and according to the Franck-Condon principle, the transition is strong as r'' (internuclear distance at the lowest state) is 3.07×10^{-8} cm., and r' (internuclear distance at the excited state) is 3.66×10^{-8} cm., so the transition $n''=0$ to $n'=8$ is the most probable. According to the arguments presented here, no other line (or band) of Na₂ is likely to occur among the interstellar lines.

Merrill's other line ($\lambda 5780$) may be provisionally identified with a line of NaK ($n''=0, n'=5$), though in this case the identification is less sure.

The molecule which is likely to be most abundant in interstellar space is H₂, but as it gives absorption lines only in the Lyman region, there is no possibility of our being able to prove its existence, but lines due to hydrides may be found amongst interstellar lines.

Department of Physics,
University, Allahabad.
April 6.

¹ NATURE, **139**, 247 (1937).² Pub. Ast. Soc. Pac., **49**, 26 (1937).³ Pub. Ast. Soc. Pac., **48**, 179 (1936).

67. ON PROPAGATION OF ELECTRO-MAGNETIC WAVES THROUGH THE ATMOSPHERE

M. N. SAHA AND R. N. RAI

(*Proc. Nat. Inst. Sci. Ind.*, **3**, 359, 1937)

(*Read March 25, 1937*)

§1. INTRODUCTION

The subject of propagation of electromagnetic waves through the atmosphere is mostly treated in terms of the ray method. The present state of our knowledge is summarized in two excellent reports: (1) Report on the present state of our knowledge of the Ionosphere by S. K. Mitra published in the *Proceedings of the National Institute of Sciences of India*, Vol. I, No. 3, December 1935; hereafter referred to as Report 1; (2) Radio Exploration of the Upper Atmospheric Ionisation by E. V. Appleton in the *Reports on the Progress of Physics*, Vol. II, 1936; hereafter referred to as Report 2. Prof. Appleton remarks on page 133 of Report 2:

‘The discussion in the present section has so far been written in terms of a ray treatment. But it is well known that it is not possible adequately to describe optical phenomena in terms of geometrical optics when the refractive index μ varies appreciably within a wavelength in the medium in a direction normal to the wavelength. Now for total reflection at normal incidence, the wavelength becomes infinitely large as $\mu \rightarrow 0$, so that in this case the ray treatment needs further justification.’

The wave treatment of the problem has been tried by Hartree¹ in three important papers. In the first paper, he obtained, in the absence of the magnetic field, the differential equations for wave propagation and calculated the electric and magnetic fields. In the second, he derived an expression for μ , taking the earth's magnetic field into account. In the third paper, he obtained approximate expressions for the optical and equivalent paths for a stratified medium in which μ varies slowly. Reviewing the work of Hartree, Appleton says [Report 2, p 133], ‘On the whole, however, it may be said that the work of Hartree shows that the errors made in using a ray treatment are not serious in most practical problems.’

It is, however, not difficult to find illustrations which show the complete insufficiency of the ray treatment even for cases ordinarily met with: as an illustration, let us take the condition of reflection. A wave propagated vertically upwards is supposed to be reflected from the spot where

the refractive index μ reaches the value 0, on account of increase in electron or ion concentration.

As Appleton has shown (see Report 1, p. 142, figs. 3-8), where q is plotted against electron-concentration, this criterion gives us the conditions of reflection of the o -wave ($p^2 = p_o^2$), as well as of the x -wave ($p_o^2 = p^2 \pm p p_h$). But μ can be zero, only if the collision frequency can be neglected. In general, however, the collision frequency is never zero, and the refractive index is complex, of the form $q = \mu + i\chi$, where χ depends on the collision frequency and the ion-concentration and is not zero at any height excepting the lowest, so that q can never take a negative value even if the real part $\mu = 0$. For example, see the q -curves drawn by M. Taylor² and Gobau³. They have shown that q takes up a steady, small, positive value with increasing values of ion-concentration, due to finite value of χ . It may be mentioned, however, that according to the magneto-ionic theory, both μ and χ are functions of ion-concentration, and of the collision frequency ν , each of which again is a function of the height z . None of the curves drawn either by Taylor or Gobau represents the actual variation of q with z . For this purpose, the best course would be to make use of a three-dimensional representation with

electron-concentration $\left(p_o^2 = \frac{4\pi N e^2}{m}\right)$ along the x -axis, ν =collision frequency along the y -axis and q along the z -axis; p^2 and ν are to be given all possible values, we get a surface representing q , and the actual (q, z) curve for the atmosphere is obtained by taking a section of this surface through points which represent the actual values of ν , and p_o^2 at a point z in the atmosphere. This has not yet been attempted, but it can be shown that q can actually never become zero. In the F -layer, there is probably some justification for neglecting collision as $\nu/p \simeq 10^{-3}$, but this cannot be said of the E -layer where $\nu/p \simeq 1$.

On account of these difficulties, several workers have tried to formulate other criteria for the reflection of waves. Booker⁴ says that appreciable reflection of an incident wave can take place only from such stratum, where either

the variation of q per unit wavelength is considerable or $q \neq 0$. One of us⁵ has shown that a better criterion for reflection is that group-velocity should be zero. This criterion can, however, in the present state of our knowledge be used only when collisions can be neglected, for Rayleigh's theorem that group velocity $u = \frac{\delta\nu}{\delta k}$, where ν = frequency, k = wave number, holds only when the waves constituting a group are undamped. We are not aware of any work which treats satisfactorily the case when the component waves are damped. However, neglecting collisions, one of us, Rai⁶, found that the criterion group-velocity $\mu = 0$ for reflections gives us the following four conditions for reflection:—

$$\left. \begin{array}{ll} (\alpha) p_o^2 = p^2 - pp_h & \dots\dots\dots x\text{-wave} \\ (\beta) p_o^2 = p^2 \cdot \frac{p^2 - p_L^2}{p^2 - p_h^2} & \dots\dots\dots x\text{-wave} \\ (\gamma) p_o^2 = p^2 & \dots\dots\dots o\text{-wave} \\ (\delta) p_o^2 = p^2 + pp_h & \dots\dots\dots x\text{-wave} \end{array} \right\} \dots\dots (1)$$

Condition (β) is new and is not given by the hitherto assumed condition for reflection, i.e. $\mu = 0$. The actual existence of reflection (β) was detected at Allahabad by Pant and Bajpai⁶, and, in fact, gave occasion for a revision of our ideas regarding the criterion for reflection.

The cases (α) to (δ) have been further discussed in a paper by Bajpai and K. B. Mathur⁷. For the sake of illustration, we may work out from their paper the electron concentration required for the above four modes of re-

flection, taking $p = 23.3$ kilocycles, $f = \frac{23.3}{2\pi} = 3.70$,

we find that

$$\left. \begin{array}{llll} \text{Reflection } (\alpha) & \text{takes place when } N = 0.88 \times 10^5/\text{cm}^3 \\ (\beta) & \text{,, ,, ,, } N = 1.40 \times 10^5/\text{cm}^3 \\ (\gamma) & \text{,, ,, ,, } N = 1.52 \times 10^5/\text{cm}^3 \\ (\delta) & \text{,, ,, ,, } N = 2.40 \times 10^5/\text{cm}^3 \end{array} \right\} \dots\dots (2)$$

The question now arises how the same x -wave can get reflected from three different strata at one and the same time. If a wave is propagated vertically upwards, it gets split up into an o -wave, and an x -wave, which are propagated with different velocities in the ionosphere. On reaching the level where $N = 0.88 \times 10^5/\text{cm}^3$, the x -wave gets reflected. *But is this reflection complete or partial?* According to the ray treatment this should be complete, as the vanishing of group-velocity means that there is no further forward propagation of energy by the waves. But Pant and Bajpai⁶ in this laboratory noticed the reflection of the x -wave according to the method (β) , and Toshniwal⁸ observed a threefold splitting of the wave, presumably of the x -wave, one of which he interpreted as mode (β) . This observation was later verified by Leiv Harang⁹ and recently all the four conditions of reflection have been verified by R. Jouaust and his co-workers. These cases

show that reflection according to (α) is incomplete, even when we get the requisite electron-concentration, and the x -wave can sometimes leak through the layer, and get reflected under conditions which are still to be investigated, from the higher regions (β) and (δ) . These cases therefore call for a revision of the treatment which has so far been pursued. But these are not the only cases which call for a revision of the ray treatment. Another is the existence of simultaneous reflection from layers at widely different heights. The best known example of this type is afforded by the case of the so-called sporadic E -layer reflection, also called Abnormal Region E -ionization by Appleton (for a detailed account, see Report 2, p. 159, where a reference to original papers will be found). It was first discovered in 1930 that 'echo-reflection often occurs from an atmospheric level approximately to that of region E for electric wave frequencies which are higher than the critical frequency for the normal region E '. Appleton concluded that 'either the recombination of ions is prevented or there is some ionizing agent present which can influence the dark side of the earth'.

The sporadic E -layer ionization has since been investigated by a large number of workers—Schafer and Goodall, Ranzi, Ratcliffe and White, Appleton and Naismith¹⁰—with the object of finding out the conditions which give rise to the formation of the layer. It was first supposed that either thunderstorms or magnetic storms may give rise to a thin but concentrated layer of electrons at the E -height, but Kirby and Judson¹¹ have shown that the phenomenon cannot be due to extra-ionization produced by thunderstorms either occurring locally or within a radius of 300 Km., or due to magnetic storms. Berkner and Wells¹² have also confirmed this finding, and have further shown that sporadic E -reflection appears to be increasing in frequency as we proceed from the magnetic equator to the poles. This has been confirmed by L. Harang.¹³ Apparently, the sporadic layer is formed by some focussing action of the earth's magnetic field on the electrons at the E -layer. But we are not concerned in this paper with the causes giving rise to the sporadic E -layer but with the phenomenon that the same wave can get reflected from this layer, which is at the height of 100 Km., as well as from the much higher F -layer at one and the same instant (of course neglecting the time of transit).

The apparent explanation seems to be that a layer of electrical particles of abnormal density but extreme thinness is formed at the height of the normal E -layer. This layer reflects partly the energy of the waves, but part of the energy of the incident waves leaks through the layer, and gets reflected from the upper F_2 -layer. This phenomenon cannot be understood if $\mu = 0$ is taken as the condition of reflection, for then reflection from the lower layer would be complete.

The M -reflections. Another phenomenon which points

to the same conclusion is the existence of M -reflections investigated by Ratcliffe and White¹⁴ and by Zenneck and Gobau. In this case the wave penetrates the E -layer, gets reflected from the F -layer, but the returned wave, instead of proceeding straight to the ground, gets reflected from the top of the E -layer, again gets reflected from the F -layer, and then proceeds straight to the ground. This phenomenon and the related E and F reflections show that the same wave can partly be reflected and can also leak through the same layer.

Let us see how all these phenomena can be explained.

§ 2.

For carrying out the programme sketched in §1, we have to start from the original Maxwellian equations, and derive equations for the propagation of electric and magnetic vectors associated with the electro-magnetic wave in the atmosphere, taking the effect of ion-concentration, collision and the earth's magnetic field into consideration. This has been done in a separate paper; here only the results which will be necessary for the present discussion are quoted: We consider only vertical propagation (axis of z). Let (E_x, E_y) , (H_x, H_y) denote the components of the electric and magnetic vectors associated with the signal. We further take the magnetic meridian as our plane of xz . Then it can be shown that the wave equations for their propagation are given by

$$\left. \begin{aligned} \frac{dE_x}{dz} &= -\frac{1}{c} \frac{dH_y}{dt}, \quad \frac{dE_y}{dz} = \frac{1}{c} \frac{dH_x}{dt} \\ \frac{dH_x}{dz} &= \frac{iL}{c} \frac{dE_x}{dt} + \frac{K_2}{c} \frac{dE_y}{dt} \\ \frac{dH_y}{dz} &= -\frac{K_1}{c} \frac{dE_x}{dt} - \frac{iL}{c} \frac{dE_y}{dt} \end{aligned} \right\}, \quad \dots (3)$$

where K_1, K_2 are complex dielectric constants. L may be called mutual dielectric constant. Further, these quantities satisfy the equations

$$\left. \begin{aligned} \frac{d^2 E_x}{dz^2} &= \frac{K_1}{c^2} \frac{d^2 E_x}{dt^2} - \frac{iL}{c^2} \frac{d^2 E_y}{dt^2} \\ \frac{d^2 E_y}{dz^2} &= \frac{iL}{c^2} \frac{d^2 E_x}{dt^2} + \frac{K_2}{c^2} \frac{d^2 E_y}{dt^2} \\ \frac{d^2 H_x}{dz^2} &= \frac{K_2}{c^2} \frac{d^2 H_x}{dt^2} - \frac{iL}{c^2} \frac{d^2 H_y}{dt^2} \\ \frac{d^2 H_y}{dz^2} &= \frac{iL}{c^2} \frac{d^2 H_x}{dt^2} + \frac{K_1}{c^2} \frac{d^2 H_y}{dt^2} \end{aligned} \right\}, \quad \dots (4)$$

We can write out values of K_1, K_2, L in the general case by using the following notations, which as far as possible conform to those used by Appleton and Ratcliffe, and Mitra in their respective reports.

h Earth's magnetic field, components h_x, h_y, h_z .

p_h Larmor Frequency. $\dots \frac{eh}{mc}$.

p_x, p_y, p_z Components of Larmor Frequency.

p Pulsatance of the E.M. Wave.

$p_0^2 = \frac{4\pi N e^2}{m}$ Where N is the number of electrons or ions per c.c. e, m are their charge and mass.

ν Collision frequency for electrons or ions.

$(\omega_x, \omega_y, \omega_z) = \frac{1}{p} (p_x, p_y, p_z)$, ω = resultant of $(\omega_x, \omega_y, \omega_z)$

$$= \frac{p_h}{p} = \frac{eh}{mcp}$$

$$r = \frac{p_0^2}{p^2} = \frac{4\pi e^2}{mp^2} \cdot N.$$

$$\beta = 1 - \frac{i\nu}{p} = 1 - i\delta, \quad \delta = \frac{\nu}{p}.$$

q = complex refractive index = $\mu + i\chi$.

We have in general when damping is not neglected

$$\left. \begin{aligned} K_1 &= 1 - r \cdot \frac{\beta^2 - r\beta - \omega_x^2}{C'}, \quad K_2 = 1 - r \cdot \frac{\beta^2 - r\beta}{C'} \\ C' &= \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega_z^2), \quad L = \frac{-r(\beta - r)\omega_z}{C'} \end{aligned} \right\} \dots (5)$$

The general solution of equations (3) and (4) is very much complicated and is not attempted here. We take the simplified case when collisions can be neglected, i.e. $\beta=1$. In this case we have

$$\left. \begin{aligned} K_1 &= 1 - r \cdot \frac{1 - r - \omega_x^2}{(1 - \omega^2) - r(1 - \omega_z^2)}, \\ K_2 &= 1 - r \cdot \frac{1 - r}{(1 - \omega^2) - r(1 - \omega_z^2)}, \\ L &= -\frac{r(1 - r)\omega_z}{(1 - \omega^2) - r(1 - \omega_z^2)}. \end{aligned} \right\} \dots (6)$$

For the solutions of equations (3) and (4), we may first utilize the facts that every quantity E or H is proportional to exp. (ipt) —then bearing in mind that E_x, E_y are now only functions of z , and introducing a new variable

$u = \frac{zp}{c}$, we have

$$\left. \begin{aligned} \frac{dE_x}{du} &= -iH_y; & \frac{dE_y}{du} &= iH_x \\ \frac{dH_x}{du} &= -LE_x + iK_2E_y; & \frac{dH_y}{du} &= -iK_1E_x - LE_y \\ \frac{d^2 E_x}{du^2} &= -K_1E_x + iLE_y; & \frac{d^2 E_y}{du^2} &= -iLE_x - K_2E_y \\ \frac{d^2 H_x}{du^2} &= -K_2E_x - iLE_y; & \frac{d^2 H_y}{du^2} &= iLE_x - K_1H_y \end{aligned} \right\} \dots (7)$$

[The last two equations in H_x, H_y are strictly not quite rigorous].

In the solution of these equations, we may as a first step regard the quantities K and L as constants, i.e., not varying with z , and then we get all the results deduced by

Appleton and others regarding splitting of the waves into o and x -components, their polarization, refractive indices, and the conditions for reflection [conditions (α) , (γ) , (δ)]. When the expressions (5) are utilized, the usual expressions for refractive index, and absorption coefficient of the two components can also be deduced.

But a little reflection shows that this procedure is not strictly justified, for K and L , both involve r and ν (ionization and collision frequency) and these vary with height. We are therefore, in general, not justified in proceeding with the solution on the assumption that K and L are constants.

To illustrate this point, let us take the simplest possible case, *viz.*, that of propagation in the magnetic equator. We have then $\omega_z=0$, $\omega_x=\omega$. We have therefore

$$K_1 = 1 - r, \quad K_2 = 1 - \frac{r(1-r)}{(1-r)-\omega^2}, \quad L=0 \quad \dots (8)$$

The equations reduce to:

$$\left. \begin{aligned} o\text{-wave: } \frac{d^2 E_x}{du^2} + (1-r)E_x &= 0; \quad \frac{d^2 H_y}{du^2} + (1-r)H_y = 0 \\ x\text{-wave: } \frac{d^2 E_y}{du^2} + \left\{ 1 - \frac{r(1-r)}{(1-r)-\omega^2} \right\} E_y &= 0 \\ \frac{d^2 H_x}{du^2} + \left\{ 1 - \frac{r(1-r)}{(1-r)-\omega^2} \right\} H_x &= 0 \end{aligned} \right\} \dots (9)$$

For the o -wave, it is usual to take $1 - \frac{p_0^2}{p^2}$ as equal to μ^2 , and the vanishing of this gives us the condition for reflection of the o -wave: *viz.* $p_0^2 = p^2$; similarly we may take

$$\mu_x^2 = 1 - \frac{r(1-r)}{(1-r)-\omega^2} \text{ and this vanishes when } p_0^2 = p^2 \pm p p_h.$$

But since r is a function of z , the procedure is not justified. We cannot, in fact, talk of a refractive index in the usual sense. These equations are of the form

$$\frac{d^2 \phi}{du^2} + k^2 \phi = 0 \quad \dots \dots \dots (10)$$

where k^2 is not a constant, but a function of (u) .

Equations of this type were first discussed by Lord Rayleigh¹⁵; see 'On the propagation of waves through a stratified medium with special reference to the question of reflection.' The following treatment is based on Lord Rayleigh's with the necessary modification. The same treatment was later given by Gans¹⁶, apparently without a knowledge of Rayleigh's previous work. It may also be mentioned that Gamow¹⁷ has used the same method in his famous work on the 'Penetration of the Potential Barrier of Nuclei of Atoms by high energy particles.'

Let us put $\phi = e^{s(u)}$. We have then

$$\frac{d\phi}{du} = \phi \frac{ds}{du}, \quad \frac{d^2 \phi}{du^2} = \left\{ \frac{d^2 s}{du^2} + \left(\frac{ds}{du} \right)^2 \right\} \phi \quad \dots (11)$$

The differential equation (10) takes the form

$$\frac{d^2 s}{du^2} + \left(\frac{ds}{du} \right)^2 + k^2 = 0 \quad \dots \dots \dots (12)$$

If it is possible to neglect the first term with respect to the second, *i.e.* if

$$\left| \frac{\frac{d^2 s}{du^2}}{\left(\frac{ds}{du} \right)^2} \right| = \left| \frac{d}{du} \cdot \frac{1}{\frac{ds}{du}} \right| \ll 1, \text{ we have} \\ \left(\frac{ds_1}{du} \right)^2 + k^2 = 0 \quad \dots \dots (13)$$

Here s_1 denotes the first approximation to s . We have then

$$\frac{ds_1}{du} = \pm ik, \text{ or } \pm l,$$

$$\text{and } \phi = C \exp. \left[\pm i \int_{u_1}^{u_2} k du \right], \text{ or } C \exp. \left[\pm \int_{u_1}^{u_2} l du \right] \dots (14)$$

The second form holds when k^2 is negative $= -l^2$.

Let us now work out a second approximation. We now regard C as varying with u or z . It can be easily shown that C satisfies the equation

$$\frac{d^2 C}{du^2} + 2ik \frac{dC}{du} + ik' C = 0, \quad \dots \dots (15)$$

$$\text{where } k' = \frac{dk}{du}.$$

If we suppose that $\frac{d^2 C}{du^2}$ can be neglected, we easily obtain from (15)

$$C = \frac{A}{\sqrt{k}} \text{ or } \frac{A'}{\sqrt{l}},$$

according as k^2 is positive or negative.

So the second approximation gives us, as the solution of (10)

$$\phi = \frac{A}{\sqrt{k}} e^{\pm i \int k ds}, \quad \dots \dots (16A)$$

$$\text{or } \frac{A'}{\sqrt{l}} e^{\pm \int l ds}. \quad \dots \dots (16B)$$

This solution can be regarded as correct if

$$\frac{d^2}{dz^2}(k^{-1}) = 0 \quad \dots \dots (17)$$

We shall assume that this condition is satisfied, though actually, as can easily be seen this is strictly not the case even approximately. Let us now see how these solutions can be applied to the present case. As the wave moves up in the atmosphere, $r = \frac{4\pi e^2}{mp^2}$. N gradually approaches the value 1, and ultimately may exceed 1, so that $k^2 = 1 - r$ becomes negative. The actual state of affairs is represented in Fig. 1. Here the abscissa ' Z ' represents height, the ordinate $r = \frac{4\pi e^2}{mp^2}$. N is proportional to the electron-concentration. The distribution of electrons is represented by the curve OPQR which is of course fancied. If wave of some other frequency were employed, the position of the line $r=1$ (A, A_1, A_2, A_3) would shift with

respect to the curve, *e.g.* for $p_1 > p$ the line would go up, and ultimately may cross over the crest of the curve OPQR. For $p_2 < p$ the line AA₁A₂ would move down as shown in Fig. 1.

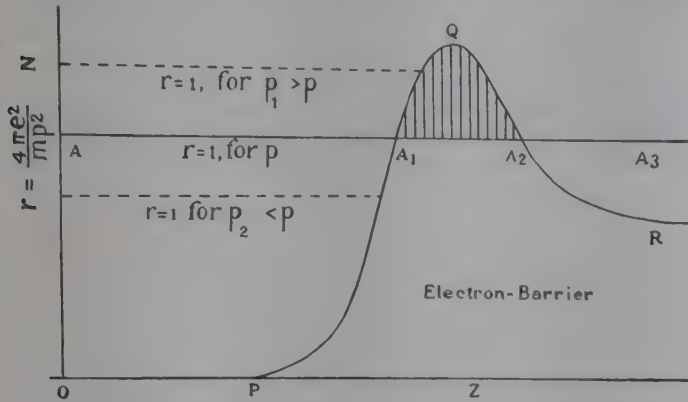


Fig. 1

From A to A₁, the value of $k^2 = 1 - r$ is positive, at A₁ it becomes zero, between A₁ and A₂ it is negative, and then it is again positive. We have to write different suitable solutions of (10) for the three different regions, and apply the conditions of continuity (equality of ϕ and $\frac{d\phi}{du}$) at the transition points A₁ and A₂. Then it can be easily shown that there is a forward and backward wave of type (16A) in the region between O and A₁, in the region A₁A₂, the disturbance is damped (16B) and there are two components, beyond A₂ there is only one wave (16A) with the negative sign. The coefficient of transmission through the barrier is given by

$$T = 4 \left(\frac{1-r_1}{1-r_2} \right)^{\frac{1}{2}} e^{-\int_{u_1}^{u_2} \sqrt{1-r} \cdot du}, \quad \dots (18)$$

where r_1 is the limiting value of r in the region (OA₁), r_2 in the region A₃. u_1, u_2 are the co-ordinates for the points A₁, A₂ respectively. We have, restoring the old co-ordinates

$$T = 4 \left(\frac{p^2}{p_0^2 - p_0^2} \right)^{\frac{1}{2}} \exp. \left[-\frac{1}{c} \int \sqrt{p_0^2 - p^2} \cdot dz \right]_{z_1}^{z_2}. \quad (19)$$

We shall try to calculate its value in some representative cases. In the equation (19), $p_0^2 = \frac{4\pi e^2}{m} \cdot N$, where N is the actual electron-concentration at a height z within A₁A₂. As ' p ' is fixed, we can put $\frac{4\pi e^2}{mp^2} = N_1$, so N is the electron-concentration at the layer where reflection takes place. Hence the index of e in (19) is given in the case of electrons by

$$-\frac{1}{c} \left(\sqrt{\frac{4\pi e^2}{m}} \right) \int_{z_1}^{z_2} \sqrt{N_0 - N_1} \cdot dz \\ = -1.9 \times 10^{-6} \int_{z_1}^{z_2} \sqrt{N - N_1} \cdot dz, \quad \dots (20)$$

and m refers to electrons. If they refer to ions, we have

$$\text{the index} = -8.3 \times 10^{-9} \int_{z_1}^{z_2} \sqrt{N - N_1} \cdot dz. \quad \dots (21)$$

The value of the integral cannot be obtained unless we know the form of the electron-concentration curve above the line $r=1$. Let us suppose that it is in the form of an isosceles triangle, so that for the rising half,

$$N = N_1 + \alpha(z - z_1),$$

then the value of N at the peak will be N_m . Then the half-breadth of the barrier $= \frac{N_m - N_1}{\alpha}$. For the descending half, $N = N_m - \alpha z$. We must have some idea of the values of N_1, N_2, α and the half-breadth in order to be able to make some calculations.

It is well known, however, that for the *E*-layer, α is large, and the thickness of the layer is small, while for the *F*-layer, α is small, and the thickness of the layer is large. But as figures are available only for the *F*-layer, we shall give a calculation based on data for *F* alone.

In a case cited by Appleton, the values of N are given as follows:—

Penetration Frequency for

$$(h = 300 \text{ Km.}) = 4 \text{ megacycles, } N = 1.98 \times 10^5$$

$$(h = 210 \text{ Km.}) = 3.7 \quad \quad \quad N = 1.70 \times 10^5$$

$$\text{So we have } \frac{dN}{dz} = \frac{2.8 \times 10^4}{90 \times 10^5} = 3 \times 10^{-3} \text{ electrons per cm.} \\ = -1.90 \times 10^{-6} \alpha^{\frac{1}{2}} b^{\frac{2}{3}} \frac{4}{3},$$

where b = half breadth of the barrier.

Using these values we have the index

$$= -1.90 \times 10^{-6} \alpha^{\frac{1}{2}} b^{\frac{2}{3}} \frac{4}{3},$$

where b = half-breadth of the barrier.

Taking into account the factor $\left(\frac{p^2}{p_0^2 - p_0^2} \right)^{\frac{1}{2}}$, we find that the amount of energy transmitted falls to half of its value, for a barrier of the form shown in fig. 1, and for gradient and electron density characteristic of the *F*-layer, if the half-breadth of the layer is about 1.5 Km. This calculation is of course fancied, but it shows that the wave can penetrate some thicknesses of the ionized layer without appreciable diminution in intensity. For the *E*-layer, α is larger, but b is smaller, hence if the thickness of the layer is of the order of a kilometer a part of the energy of the incident wave may be transmitted, though the value of μ is zero for the wave transmitted at the point where it meets the electron-barrier.

This treatment of penetration of electron or ion-barriers by e.m. waves cannot be utilized for the *x*-wave, which has singularities at

$$(\alpha) p_0^2 = p^2 - p p_h, \quad (\beta) p_0^2 = p^2 \cdot \frac{p^2 - p_h^2}{p^2 - p_h^2}, \text{ and}$$

$$(\delta) p_0^2 = p^2 + p p_h.$$

The problem is still under consideration.

In conclusion, we wish to express our thanks to Dr. G. R. Toshniwal for many useful discussions and to Mr. K. B. Mathur and Dr. Rakshit for much help in the calculations.

SUMMARY

In this paper, the ray treatment of passage of e.m. waves through the ionosphere has been critically reviewed, and a wave treatment has been given for the σ -wave for propagation in the magnetic equator. It has been shown that contrary to the implicit assumption in the ray treatment which requires complete reflection at the point in the ion-barrier where μ falls to zero, there may be considerable penetration by the wave of the barrier, even when the thickness of the barrier amounts to several kilometres.

REFERENCES

- ¹ HARTREE, *Proc. Camb. Phil. Soc.*, Vol. 25, p. 47, (1929) and Vol. 27, p. 143, (1931); *Proc. Roy. Soc.*, Ser. A, Vol. 131, p. 428, (1931).

- ² M. TAYLOR, *Proc. Phys. Soc. Lond.*, Vol. 45, p. 245, (1933); Vol. 46, p. 408, (1934).
- ³ GOBAU, *Zeits. f. H. F. T.*, Vol. 45, p. 181, (1935).
- ⁴ BOOKER, *Proc. Roy. Soc.*, Ser. A, Vol. 150, p. 267, (1935); Vol. 155, p. 235, (1936).
- ⁵ R. N. RAI, *Proc. Nat. Inst. Sci. India*, Vol. III, p. 307, (1937).
- ⁶ PANT AND BAJPAI, *Science and Culture*, Vol. 2, p. 409, (1937).
- ⁷ BAJPAI AND MATHUR, *Ind. Jour. Physics* (in course of publication).
- ⁸ TOSHNIWAL, *Nature*, Vol. 135, p. 471, (1935).
- ⁹ L. HARANG, *Terr. Mag.*, Vol. 40; R. Jouaust, Abadie and Joigny, *L'onde électrique*, Vol. 16, p. 185, (1937).
- ¹⁰ For full reference, see Report 2.
- ¹¹ KIRBY AND JUDSON, *Journ. Res. Bur. Stand.*, Vol. 14, (March, 1935).
- ¹² BERKNER AND WELLS, *Terr. Mag.*, Vol. 42, p. 73, (1937).
- ¹³ L. HARANG, *Terr. Mag.*, Vol. 42, p. 55, (1937).
- ¹⁴ RATCLIFFE AND E. L. WHITE, *Phil. Mag.*, Vol. 16, p. 125, (1933); Gilliland, *Journ. Res. Bur. Stand.*, Vol. 14, p. 184, (1935).
- ¹⁵ LORD RAYLEIGH, *Collected Scient. Papers*, Vol. VI, p. 475.
- ¹⁶ GANS, *Ann. d. Phys.*, Vol. 47, p. 130, (1915).
- ¹⁷ GAMOW, *Constitution of Atomic Nuclei and Radioactivity*: Second Edition.

68. ON THE ACTION OF ULTRA-VIOLET SUNLIGHT UPON THE UPPER ATMOSPHERE

(*Proc. Roy. Soc. Lond.*, **A160**, 155, 1937)

(Received 19 August 1936)

I—INTRODUCTION

The ordinary solar spectrum extends, as is well known, to about $\lambda 2913$, the more ultra-violet parts being cut off by ozone absorption in the upper atmosphere. We have thus no direct knowledge of the distribution of intensity in the solar spectrum beyond $\lambda 2913$, as it will appear to an observer situated outside the atmosphere of the earth. But it is now recognized that a number of physical phenomena is directly caused by the photochemical action of this part of sunlight on the constituents of the upper atmosphere. Such phenomena are (1) the luminous spectrum of the night sky and of the sunlit aurora,¹ (2) the ionization in the E, F and other layers which is now being intensely studied by radio-researchers all over the world², (3) the formation and equilibrium of ozone (see Ladenburg 1935), (4) magnetic storms and generally the electrical state of the atmosphere.

Formerly it was a debatable point whether some of these phenomena were not to be ascribed to the action of streams of charged particles emanating from the sun. There seems to be no doubt that the polar aurora and certain classes of

magnetic storms are to be ascribed to the bombardment of molecules of N_2 and O_2 by such charged particles, for these phenomena show a period which is identical with the eleven year period of the sun, and are found in greater abundance, the nearer we approach the magnetic poles.³ But there now exists no doubt that the ionization observed by means of radio-methods in the E and F_1 regions, their variation throughout day and night, and at different seasons is due to the action of ultra-violet sunlight. This was decisively proved by observations during several total solar eclipses since 1932 (Appleton and Chapman 1935). The luminous night-sky spectrum, though it has certain points of similarity to the polar aurora, is on the whole widely different, and is found on nights free from electrical disturbances. The prevailing opinion is that it is mainly due to the ultra-violet solar rays, i.e. in the course of the day sunlight is stored up by absorption by the molecules in the upper atmosphere, and again given up during the night, in one or several steps, as a fluorescence spectrum. According to S. Chapman (1930) the formation of the ozone layer and its equilibrium under different seasonal conditions is

¹ For a general account of the spectrum of the luminous night sky, see Dejjardin (1936).

² For general information regarding investigation on the ionosphere, see Mitra and others (1936) and Appleton (1936).

³ See for general information article by Störmer (1931). The frequency of aurorae appears to reach a maximum 20° from the magnetic pole.

also to be mainly ascribed to the action of ultra-violet sunlight. In the following paper an attempt will be made to discuss some of these questions in as rigorous a way as is possible with our present knowledge. It is evident that an adequate discussion is possible only if we have a good knowledge of (1) the distribution of intensity in the solar spectrum beyond $\lambda 2900$, (2) the photochemical action of light of shorter wave-length than $\lambda 2900$ on the constituent molecules of the upper atmosphere, which are mainly oxygen and nitrogen. We shall first consider (1).

2—THE ULTRA-VIOLET SPECTRUM OF THE SUN

The disappearance of sunlight below $\lambda 2900$ has long been known, through the researches of Fowler and Strutt (1917), and of Fabry and Buisson (1913) and others, to be due to the absorbing action of a layer of O_3 (equivalent in amount to a 3 mm. column at N.T.P.) formed in the upper atmosphere. The long series of works by Götz, Meetham and Dobson (1934) and Regener (1934) have shown that this layer extends from about 20 km., reaches a maximum concentration at 30 km., and probably does not extend much beyond 50 km. But, as we shall see presently, the principal photochemical reactions in N_2 and O_2 , including ionization, are produced only by light of wave-length < 3000 Å, and hence in order that a correct estimate may be made of the action of sunlight on O_2 and N_2 gas above the ozone layer, it is necessary for us to have a detailed knowledge of the emission of the sun below $\lambda 3000$ Å. In the absence of direct knowledge, recourse is made to extrapolation, i.e. emission below $\lambda 3000$ Å is supposed to be identical with that of a black body at 6800°K . The justification for such an assumption is found in the work of H. H. Plaskett⁴ and Fabry that the intensity distribution in the solar spectrum in regions free from any absorption lines agrees very well with that of a black body at 6800°K . But this evidence is at best indirect, and many observers hold that solar emission in the ultraviolet is subject to a good deal of fluctuation and differs widely from that of a black body.⁵

⁴ For detailed report on this very intricate problem, and generally on the temperature of stars, see Brill (1932); for later work, see the same, *Ergänzungsband*, 7, but usually discussion is confined only to available radiation from stars.

⁵ The opinion that the ultra-violet radiation from the sun differs widely from that of a black body at 6800°K . has been expressed by many workers, from different points of view. Petit (1935) finds, from actual measurements between $\lambda\lambda 4100$ – 3000 , that the emission curve shows no resemblance to that of a black body.

Mulders (1935) finds that the solar emission curve (when corrected for absorption) shows a form which bears no resemblance to a black-body curve. From $\lambda 9500$ to $\lambda 4100$ it approximates a black-body curve at 7140°K , but between $\lambda\lambda 4000$ – 3000 it approximates a black body curve at 4800°K . These determinations are subject to a good deal of uncertainty, as no account is taken of absorption by O_2 and N_2 in the uppermost layers, as described in the present paper, and therefore they do not apply to the region discussed in this paper.

Speculations below $\lambda 3000$. To explain terrestrial magnetic storms and aurorae, Maris and Hulburt (1929) proposed a hypothesis that the sun

3—THE NEGATIVE BANDS OF NITROGEN IN THE SPECTRUM OF THE NIGHT SKY

It is now possible to produce further evidence that ultra-violet emission from the sun is widely different from black-body radiation, but we shall at the outset discuss in full only *one line of evidence which does not appear to admit of any other interpretation*. This is the appearance of the earlier members of the first negative bands of nitrogen in the spectrum of the upper atmosphere when illuminated by sunlight. These bands have the wave-lengths $\{(0, 0) - 3914\}$, and $\{(0, 1) - 4278\}$, and on unimpeachable spectroscopic grounds they have been ascribed to N_2^+ , *vide* § 6.⁶

These bands are very intense in the spectrum of the polar aurora, where they are produced by the bombardment of N_2 gas by electrons. The intensity is found to be the same as that of the green line of O, $\lambda 5577.35$. But the lines are also found in the spectrum of the night sky, though so faintly that some observers have even denied their existence in the night-sky spectrum. But the issue has been cleared up by the following observation due to Slipher (1933):

“But the negative nitrogen bands typical of auroral display spectra do not accompany this chief yellow line (green) in the sky, except when auroral displays are actually present. However, these nitrogen bands, I found, could be photographed in the morning and evening skies if brief exposure were made at the moments, when the last and first traces of sunlight touch the high atmosphere. Thus the day, as it were, begins and ends with a sort of auroral flash.”

The physical meaning of this observation becomes clear if we consider the genesis of the N_2^+ bands. For this purpose it is necessary to turn to fig. 1, which is the energy-level diagram of N_2 and N_2^+ . We notice that the first negative bands are due to transition of the electron from a level called $A'(N^4S.N^+{}^3P.B^3\Sigma)^7$ to the normal level of N_2^+ called $X'(N^2D.N^+{}^3P.^2\Sigma_g^+)$. The energies of excitation of these two levels have been obtained from both cathode-ray bombardment and from spectroscopic analysis, both of

may, from time to time, be subjected to outbursts of ultra-violet emission localized at certain points. These flares of radiation may have 10^6 times the intensity of black-body radiation between $\lambda\lambda 500$ – 1000 , according to the above-mentioned authors.

Gurney (1928) expresses the view that the solar radiation in the ultra-violet (near $\lambda 584.4$) is in excess of black-body radiation by a factor of 10^6 . In a note (Saha 1936) the present author pointed out that the flash of bands due to CO^+ and N_2^+ in the tail of comets can be explained if we suppose that the sun shoots out high energy photons and ionizes CO and N_2 in the tail in the way proposed in § 3 of this paper. In the course of a discussion, Professor H. N. Russell pointed out that once N_2 and CO are ionized, they can be maintained in excited states of N_2^+ and CO^+ by visible radiation from the sun. The subject of cometary spectra will be taken up in a subsequent paper.

⁶ For photographs of N_2^+ bands in the aurora, see Slipher and Sommer (1929); see also Slipher (1933).

⁷ This notation means that one N atom is in a 4S state, the other is singly ionized and is in a 3P state and the molecule as a whole is in a $^3\Sigma$ state, and so on.

which yield concordant values. As a glance at fig. 1 shows, the first ionization potential (excitation of the X' level) is 15.55 V, and the second ionization potential (excitation of A level) is 18.68 V. But Slipher's observation shows that the A' level of N_2^+ is produced by sunlight acting directly on the N_2 molecules of the upper atmosphere. It therefore becomes necessary to find out how these bands are produced by direct photochemical action of sunlight, without the intervention of any bombarding electron. This is furnished by the study of the absorption spectrum of N_2 by Hopfield (1930), who found a number of absorption bands at $\lambda\lambda 723, 694, 681, 675, 671$ which pass to a continuous absorption at $\lambda 660$. Mulliken (1933) shows that the most probable explanation of the origin of these bands is as follows:



i.e. one of the component atoms remains unchanged. In the other atom, one electron passes to the ns state, thus giving rise to a number of 4P terms in a Rydberg series. The limit corresponds to the state of N_2^+



which is marked by a continuous absorption at $\lambda 660$, which corresponds to the ionization of N_2 to the A level of N_2^+ . What is particularly important to notice is the fact that Hopfield did not find any trace of continuous absorption at the first ionization potential of N_2 , corresponding to the X' level.

Several investigators (for example, see Price and Collins 1930, particularly para. 2, p. 715) have subsequently found that many diatomic molecules show a similar type of strong absorption leading to one or more higher ionization potentials, the absorption leading to the lowest ionization potential being very feeble or sometimes totally absent.

Hopfield's experiment therefore proves that light of wave-length $\lambda 794$ cannot directly ionize N_2 to the N_2^+ normal state, i.e. a quantum having an energy content of 15.55 V (X' level), $\lambda 794$, has no direct action on N_2 though the energy is sufficient for raising N_2 to the lowest state of N_2^+ . But a quantum of energy content of 18.68V, $\lambda 661$, can directly ionize N_2 to the A level. This supplies the clue to the interpretation of Slipher's result. Sunlight of wave-length $< \lambda 661$ produces direct ionization of N_2 to the A state of N_2^+ , which, being excited, emits the negative bands and reverts to the normal N_2^+ state (X). This explains the flash of negative bands at sunrise and sunset. After the withdrawal of sunlight, the excited N_2^+ ions speedily revert to the normal state, and we are left only with N_2^+ normal ions. These are incapable of radiating, and in the course of the night may be neutralized by the direct capture of an electron in different excited states of N_2 , but it is quite probable that when the colliding electrons have

sufficient velocity, a number of N_2^+ (X') ions may be further excited to the A state. This process may account for the feeble emission of negative bands during the night observed by Sommer and certain other workers.⁸

4—IONIZATION OF THE NITROGEN MOLECULE IN THE UPPER ATMOSPHERE

The above arguments therefore prove in a very conclusive manner that N_2 is ionized above a height of 200 km. directly to N_2^+ by the direct action of sunlight. It is difficult to estimate the number of N_2^+ excited molecules thus produced, without photometric measurement of the intensity of the bands, and other relevant laboratory experiments. But we obtain an idea of the number of free electrons in this region from measurement of the F_2 layer ionization. This is estimated by Appleton (1936) and others to be nearly 5×10^5 electrons per c.c., and we can assume that a fair proportion of these electrons is produced by the direct ionization of N_2 to N_2^+ by the action of ultra-violet sunlight. Apart from this evidence, the very intensity of N_2^+ bands during daylight flash, and their intensification in a sunlit aurora (Störmer 1931), is definite proof that sunlight produces considerable ionization of N_2 to N_2^+ . It will now be shown that if the radiation from the sun be supposed to be the same as that given by a black body at 6500° , the number of quanta available having an energy content greater than 18.68V (excitation potential of N_2 to the A state of N_2^+) is hopelessly inadequate for the purpose. The argument is as follows:⁹

The number of quanta of frequency greater than ν , and falling normally on unit surface of the earth per sec., is given by

$$N_\nu = 3 \times 10^{17} I_1,$$

where

$$I_1 = \int_{x_0}^{\infty} \frac{x^2}{e^x - 1} dx \text{ and } x = \frac{h\nu}{KT}. \quad (1)$$

⁸ The author has discussed the line of argument followed here with many workers on the field in Europe and America, in the course of his travels during 1936, but the only serious objection against it was raised in the course of a friendly conversation with Dr Wulf, of the Bureau of Soils and Agricultural Research, Washington, D. C. Dr Wulf thinks that the ionization of N_2 to N_2^+ is due to the photons having the wave-length $\lambda 794$, corresponding to the first ionization potential of 15.55 V; the N_2^+ ions produced in this way further absorb the quanta representing the second negative bands of N_2 , and thus raise N_2^+ to the N_2^+ excited state A' . The flash of negative bands is due to fluorescence of these excited states of N_2^+ .

The mechanism of N_2^+ luminescence postulated by Dr Wulf appears unlikely, as according to the experiments of Hopfield, N_2 shows no, or extremely feeble, absorption at $\lambda 794$. If we suppose that the absorption exists at all, it must be very small, hence we should have to suppose that these rays penetrate to very low depths of the atmosphere. The observational fact that N_2^+ bands are obtained at heights exceeding 200 km. and not below, shows that the photons giving rise to N_2^+ luminescence are absorbed completely by a very small amount of N_2 . This can apply only to continuous absorption at $\lambda 660$, corresponding to the second ionization potential.

Regarding emission of N_2^+ bands by the night sky, free from aurora, evidence appears to be positive, Dejardin (1936, p. 10). The bands are extremely faint.

⁹ For further details about this calculation see Saha (1935).

For $\lambda = 660 \text{ \AA}$ corresponding to 18.68 e-volts, $I_1 = 3 \times 10^{-13}$, hence we have

$$N_v = 10^4. \quad (1')$$

So the solar rays can produce only 10^4 ions of N_2^+ (A state)/sec./cm.² in the whole depth of the atmosphere. But according to a calculation by Chapman (1931), the total number of ions to be produced per sec. for maintaining the total ionization is 3×10^{10} . Of course, the total ionization is not entirely due to N_2^+ , probably the greater part is due to ionization of O_2^+ . But the intensity of N_2^+ bands shows that at least a substantial part, say one-tenth, is due to ionization of N_2 . Hence we conclude that the solar ultra-violet light of wave-length $< \lambda 660$ is about a million times more intense than that given by a black body at a temperature of 6500°K . This conclusion, to which it is difficult to see any alternative, brings out the necessity of investigating the ultra-violet emission of the sun with greater care than has hitherto been done. From arguments which are given elsewhere, it appears probable that if we could observe the solar spectrum outside the atmosphere of the earth, it would appear very much like those of planetary nebulae, i.e. composed of a faint continuous background superimposed with bright emission lines of H, He and He^+ , Fe^+ , Fe^{++} , and other elements which are abundant in the atmosphere of the sun, and which have their resonance lines in this part of the spectrum.

Bearing these points in mind, we now turn to a critical examination of the results on the night-sky spectrum and on the ionosphere.

5—DISTRIBUTION OF ELEMENTS IN THE UPPER ATMOSPHERE

A rigorous theoretical treatment of all the upper air phenomena requires a knowledge of the distribution of elements at different heights of the atmosphere, and its variation by night and day. We shall illustrate the point by an example.

In the foregoing paragraphs, we discussed in detail the appearance of N_2^+ bands as a flash in the upper atmosphere produced by the disappearing light of the evening sky, or by the dawning light of the morning sky. Rough estimates show that the phenomenon occurs at a height of 200 km. (see DeJardin 1936, p. 10). Why does not this flash extend below? The obvious answer is that at this height solar light of wave-length $< \lambda 660$ is completely absorbed by the layer of gas traversed. We have next to link up this phenomenon with the laboratory experiments dealing with the intensity of absorption of N_2 gas at wave-lengths below $\lambda 660$. Supposing we find, from accurate laboratory experiments, that 1/500 cm. of N_2 at N.T.P. reduces the intensity of $\lambda 660$ to 1/eth of its value, and suppose we assume that the action of light is

inappreciable when the intensity falls to 10^{-3} of its primitive value. This can be achieved by $x \times 1/500$ cm. of N_2 gas at N.T.P., where $e^x = 10^3$ i.e. $x = 7$, and the thickness of gas is 0.014 cm. at N.T.P., i.e. we conclude that the amount N_2 gas traversed by sunlight at nearly horizontal incidence at a height of 200 km. is 0.014 cm. of N_2 at N.T.P., and hence there will be no ionization below 200 km.

At the present time our knowledge of the absorption coefficient of every ray below $\lambda 3000$ in O_2 and N_2 is in an extremely unsatisfactory state, but probably this will be available before long. Knowledge of this absorption coefficient will enable us to estimate quantitatively the photochemical reactions produced in the upper atmosphere, provided we have a knowledge of the distribution of the elements at different heights. We should therefore have ready for use a table which tells us of the quantity of gas of each kind (N_2 or O_2) which lies above a height z . It is usual to express this quantity in lengths, i.e. centimetres of the gas at N.T.P., 1 cm. being equal to 2.79×10^{19} mol. On the surface of the earth the quantity is given by H , the height of the homogeneous atmosphere. At any height z , let the corresponding quantity for a gas x be given by H_z^x . Then we have $H_z^x = P_z^x / \rho_0^x$, where P_z^x is the partial pressure of the gas x at height z , and ρ_0^x is the density of the gas at N.T.P. To calculate P_z^x we take the hydrodynamical equation

$$dp = -\rho g dz. \quad (2)$$

We have omitted z and x from p and ρ for the sake of elegance. Now we have

$$p = \frac{RT}{M} \rho,$$

where M = molecular weight, R = universal gas constant. Hence

$$\frac{dp}{p} = -\frac{Mg dz}{RT} \text{ or } \log_e \frac{P_z^x}{P_0^x} = -\frac{gM_x}{R} \int_0^z \frac{dz}{T}. \quad (3)$$

The integral $\int_0^z \frac{dz}{T}$ is common for all gases. Let it be denoted by β . Then we have

$$P_z^x = P_0^x e^{-\frac{gM_x}{R} \beta}, \text{ and } H_z^x = H_0^x e^{-\frac{gM_x}{R} \beta}, \quad (4)$$

where $H_0^x = \frac{P_0^x}{\rho_0^x}$ denotes the quantity of gas at N.T.P. which is equivalent to the whole column in the atmosphere.

An approximate (not accurate, but sufficient for the height considered by us) value of the integral is obtained if we know the total pressure at z , for considering that the mixture does not change much, we have

$$\log_e \frac{P_z}{P_0} = -\frac{gM}{R} \int_0^z \frac{dz}{T} = -\frac{gM}{R} \beta \quad (5)$$

$$\text{or } \beta = \frac{-R}{gM} \log_e \frac{P_z}{P_0},$$

These bands extend from $\lambda 1450$ to $\lambda 1226$, corresponding to $v''=0$. No quantitative estimate is available of the intensity of this absorption. It is stated by Lyman (1928) that 9 mm. of air at N.T.P. is sufficient to show this absorption. The bands were first obtained in absorption, and identified by Sponer.

The corresponding amount is attained at a height of about 60 km., but it is probably unnecessary to consider this absorption, as oxygen has far stronger absorption in this region. In fact, Ladenburg finds that 0.002 cm. of O_2 at N.T.P. reduces $\lambda 1450$ to one-half its strength, so it is clear that this radiation is almost completely absorbed above the E layer by oxygen molecules.

(b) The Vegard-Kaplan bands ($X'\Sigma_g \rightarrow A^3\Sigma_g^+$). These bands are given by the formula

$$\nu = 49774.4 + (1446.46\nu' - 13.93\nu'^2) - (2345.46\nu'' - 14.45\nu''^2),$$

and absorption by normal molecules should extend from $\lambda 2000$ towards the ultra-violet. But as the values of r for the normal and excited states are widely different ($r'=1.29$ cm., $r''=1.09$ cm.), transitions from $v''=0$ to some high value of v' will be more probable, according to the Franck-Condon Principle. Such bands will occur at about $\lambda 1700$.

Though no laboratory experiment has yet been done with the express intention of obtaining the absorption of Vegard-Kaplan bands, it appears that they were recorded by Hopfield (1928) some years ago. He found that with 0.06 to 19 m. of N_2 column at N.T.P., the following bands were obtained: $\lambda\lambda 1742.4$, 1728.4 , 1701.4 , 1688.3 , 1666.3 , 1650.2 . These are possibly Vegard-Kaplan absorption bands.

These wave-lengths are also strongly absorbed by O_2 , but not so strongly as $\lambda 1460$. Hence it is quite plausible that by means of this absorption, a large proportion of N_2 molecules is excited to the N_2 ($N^4S + N^2D$) $A^3\Sigma_u^+$ stage, which is the final level of the first positive bands of N_2 . It therefore appears plausible that, during daytime, a large proportion of N_2 molecules will be found in the excited state of N_2 $A^3\Sigma_u^+$, and molecules in such excited states will give rise to absorption of the first positive bands. But it is not possible to make any calculation of the proportion of such excited molecules, as all the data required for the purpose are lacking. These are (1) the intensity of solar light in the region $\lambda\lambda 2000-1700$; (2) the intensity of absorption of these bands in nitrogen gas. But the process is probably confined to over 30 km., as at this height the amount of N_2 gas is about 100 m. at N.T.P., which is the amount required for complete absorption of these bands.

As purely a tentative measure, an attempt has been made to find out whether any of the well-known N_2 band lines belonging to the first or the second positive bands, or due to N_2^+ , occur amongst the unidentified lines of the telluric part of the Fraunhofer spectrum. The results,

which are not very conclusive, will be communicated in a later paper.

THE NEGATIVE BANDS OF NITROGEN

No estimate is yet available of the intensity of continuous absorption of N_2 at $\lambda 661$ which is responsible for ionizing N_2 to the N_2^+ A' state and thus giving rise to the negative bands of N_2^+ observed in the first sunlight flash of morning or evening hours. But it appears that the N_2^+ ion is a normal constituent of the upper atmosphere during daytime, and if there be a sufficient number of them, we may obtain the strongest N_2^+ bands in the Fraunhofer spectrum as telluric lines. The relevant data will be discussed elsewhere. They are also not very conclusive.

Can nitrogen be photochemically decomposed into atoms by sunlight?

It is well known that in the case of most diatomic molecules, and particularly in the case of O_2 , a continuous absorption process is known which decomposes the molecule into a normal and an excited atom. Usually no continuous absorption is known which corresponds to the dissociation of the molecule into normal atoms. For nitrogen we can expect the following process:

$$N_2(^1\Sigma_g) + h\nu = N^4S + N^2D - E_1,$$

$$N_2(^1\Sigma_g) + h\nu = N^4S + N^2P - E_2,$$

$$E_1 = D + N^2D - N^4S = 7.32 + 2.37 \text{ V} = 9.69 \text{ e-volts} = 1273A,$$

$$E_2 = D + N^2P - N^4S = 7.32 + 3.66 \text{ V} = 10.98 \text{ e-volts} = 1124A.$$

No such continuous absorption corresponding to these processes has yet been discovered for N_2 . Hopfield noted two isolated absorptions at $\lambda 1518.02$ and $\lambda 1437.2$. The forbidden lines of nitrogen are

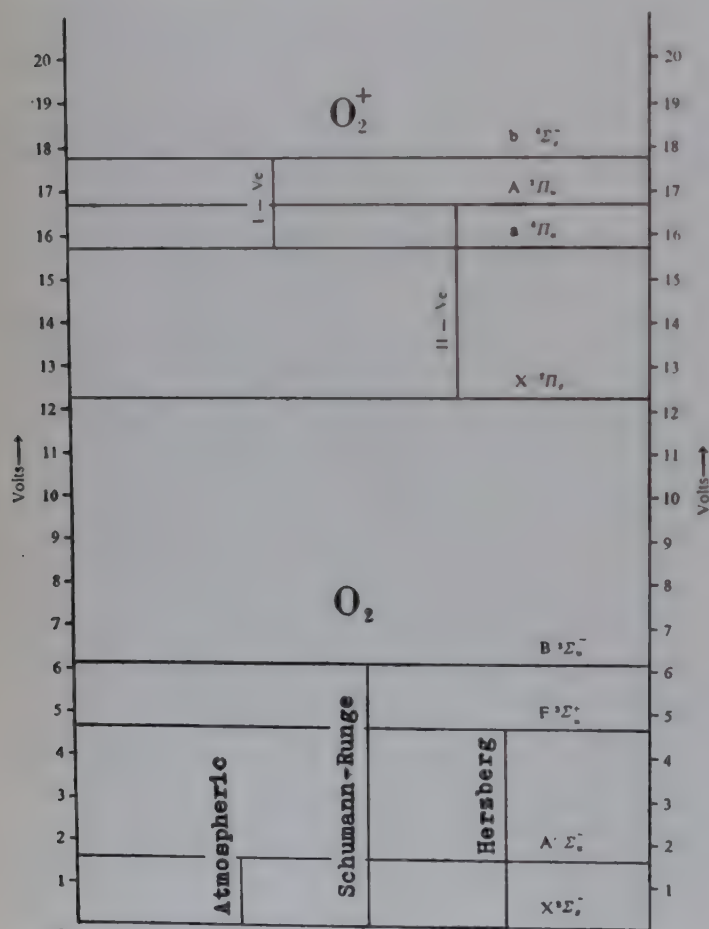
$$\begin{array}{ll} {}^4S-^2D = \nu & \left. \begin{array}{l} 19223 \\ 19231 \end{array} \right\} \lambda \begin{array}{l} 5202.1, \\ 5199.9, \end{array} \\ {}^4S-^2P = \nu & 28840 \quad \lambda 3467.4, \\ {}^2D-^2P = \nu & \left. \begin{array}{l} 9617 \\ 9606 \end{array} \right\} \lambda \begin{array}{l} 10398.3, \\ 10410.2. \end{array} \end{array}$$

The last is in the infra-red and has not yet been observed either in the morning or the evening flash. ${}^4S-^2P$, $\lambda 3467.4$, is too far in the ultra-violet and has not yet been found. ${}^4S-^2D$, $\lambda 5202$, is promising, but it is unfortunately mixed up with the (0, 2) bands of N_2^+ . Sommer (Slipher and Sommer 1929) at one time identified the line observed near $\lambda 5206$ as being the ${}^4S-^2D$ line of N, but the matter needs careful reinvestigation. The discussion shows that as yet there is no definite evidence for the presence of forbidden lines of N in the night-sky spectrum, but this does not absolutely exclude the possibility of their occurrence. [Slipher (1933) has given some very strong red and infra-red bands, without indicating their origin].

OXYGEN

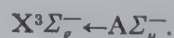
Oxygen is very interesting, as so far no band lines due to O_2 or O_2^+ have been traced in the spectrum of the night sky or the polar aurora. The Fraunhofer spectrum of the sun shows only the A, B... bands of oxygen, and the night-sky spectrum shows only the green line ($^1D_2 \rightarrow ^1S_0$), and the red lines due to the forbidden transition $^3P_{1,2} \rightarrow ^1D_2$. From these findings the conclusion has sometimes been drawn that oxygen exists in the upper atmosphere completely in the atomic state, i.e. is dissociated completely by sunlight above a certain height into atomic oxygen.

We get to a better understanding of these facts when we first critically consider the spectra of O_2 and O_2^+ , so far as they are known at the present time. Unfortunately, the knowledge, particularly beyond 1000Å, is not as complete as can be desired. Whatever is known is presented in the energy-level diagram, fig. 2, and tables.

FIG. 2¹²

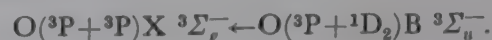
We observe that absorption by normal oxygen is confined to

(1) The atmospheric bands corresponding to the transition



These bands occur very prominently in the Fraunhofer spectrum and constitute the A, B and α bands of Fraunhofer

(2) The Schumann-Runge bands and the continuum beyond it. Of all the absorption bands of O_2 , these are the best studied. They correspond, according to Mulliken, to the transition



Beyond 11750, these bands pass into continuous absorption, corresponding, as Herzberg has shown, to the photochemical decomposition of O_2 into atoms as follows:



This absorption extends up to 11250Å. The beginning at 11750 corresponds to $7.05V = D + E$, where D is the heat of dissociation of O_2 into two normal O^3P atoms, $= 5.09V$, and E is the heat of excitation of O^3P atom to the O^1D_2 state, viz. $1.96V$. For the lower wave-lengths in the continuum, absorption denotes that the products of decomposition separate with some kinetic energy.

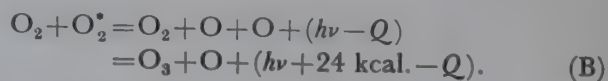
(3) A very feeble set of absorption bands, which appear to pass into a feeble continuum, has been reported by Herzberg at $\lambda\lambda 2595-2429$. The continuum at $\lambda 2429$ has been interpreted as giving rise to decomposition of O_2 into two normal O^3P atoms, for $\lambda 2429$ corresponds exactly to the dissociation potential of O_2 , viz. $5.09V$. But the intensity of this absorption is about 10^{-7} times less than that of the continuum beyond 11750, for a column of 0.002 cm. of O_2 at N.T.P. reduces $\lambda 1460$ to one-half, while 25 m. of O_2 at N.T.P. scarcely suffice to bring out the absorption of the bands at $\lambda\lambda 2595-2429$. According to Table I, this absorption may occur at about $20-40$ km., but as this is the ozone region which cuts off all light between $\lambda\lambda 2900-2300$, we need not consider it.

The three types of absorption described above give rise to three well-known processes:

(a) The Schumann-Runge absorption ($X^3\Sigma_g^- \leftarrow B^3\Sigma_u^-$). This produces ozone as follows:



where O_2^* denotes the excited state of O_2 , viz. $B^3\Sigma_u^-$. The O_2^* molecule collides with a normal O_2 molecule (collision of the second kind) and dissociates it into two atoms as follows:



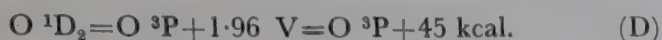
(b) The second process indicates that one of the atoms combines with O_3 to form an O_3 molecule. This process is highly probable, as the reaction is exothermic. We have, according to careful calorimetric investigations,



The energy set free is $h\nu + 24 - Q$, and if the wave-length used be $\lambda 2040$, $h\nu = 141$ kcal. Hence the energy set free is

¹² Reprinted from *Proc. Nat. Inst. Sci. Ind.* **1**, 230, 1935.

$141+24-117=48$ kcal., and this may raise the remaining O atom to the O 1D_2 state, as shown below:



This O 1D_2 atom reacts more readily with another O₂ atom and forms a second O₃ molecule and 72 kcal. of heat is produced. Thus, as Warburg experimentally established long ago, one quantum of light $< \lambda 2040$ produces two molecules of O₃.

(c) Light of wave-length $> \lambda 2040$ can also convert O₂ into O₃, but as has been shown experimentally, this is a high-pressure phenomenon. It corresponds to the Herzberg absorption at $\lambda 2425$. This probably plays no part in the formation of ozone in the upper atmosphere, and in the lower atmosphere it is ineffective owing to the fact that $\lambda \lambda 3000-2300$ is cut off by ozone.

Let us now form a rough idea of the heights at which these processes take place in the upper atmosphere. *It is easy to show that the O₃ formation and the dissociation of O₂ into atoms take place at quite different heights, and the two phenomena have no connexion with each other.* According to Kreussler (see Lyman, 1928), a length of 20 cm. of O₂ reduces $\lambda 1860$ (Schumann-Runge band) to two-thirds of its intensity. So according to Table I, $\lambda 1860$ is reduced to one-fourth of its intensity at a height of 45 km. But the other wave-lengths can be completely absorbed only at lower heights. $\lambda 1930$ loses 6.2% of its intensity by the same column, so to reduce it to one-tenth its intensity, we require a column of oxygen 840 cm. in length, and this is reached at a height of about 35 km. These calculations are rather rough, but they suffice to show that the discovery of Götz, Meetham and Dobson (1934) that the O₃ layer exists at a height of 20-50 km. is in substantial agreement with the absorption data on Schumann-Runge bands. The decomposition of O₂ into O 3P and O 1D_2 takes place at quite different heights, for as mentioned before, $\lambda 1460$ is reduced to half its strength by 0.002 cm. of O₂ at N.T.P. So this ray is reduced to 10^{-3} times its strength when the equivalent column is 0.014 cm., and Table I shows that this is accomplished at about 180 km., i.e., above the E region of the ionosphere. The Herzberg absorption at $\lambda 2429$ appears to be ineffective in producing any substantial dissociation of O₂ into atoms, as this wave-length is absorbed by the ozone layer above a height of 30 km., above which there is not sufficient oxygen which can be appreciably dissociated in this fashion.

IONIZATION OF O₂ TO O₂⁺

Let us now examine how O₂ is photo-ionized to O₂⁺. Tate and Smith (1932) have measured two ionization potentials of O₂, viz. at 12.5 and 16.1 V. Mulliken and Stevens (1933) have shown how these measurements can be reconciled with the known spectroscopic levels of O₂⁺.

The known levels of O₂ are:

(1) The first negative band between $\lambda \lambda 5300-7900$ consisting of single headed bands shaded towards the red.

According to Mecke (1927) the band heads are given by $\nu = 16592.2 + (1180.3\nu' - 17.8\nu'^2) - (1026.1\nu'' - 11.1\nu''^2)$.

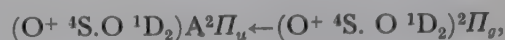
According to Mulliken and Stevens (1933) the electronic transition is



(2) The second negative bands between $\lambda \lambda 2200-4400$ consist of double bands shaded towards the red. The band heads are given by

$$\nu = 38308 + (887\nu' - 13.4\nu'^2) - (1859.9\nu'' - 16.53\nu''^2).$$

The electronic transition, according to Mulliken and Stevens, is



$r'' = 1.14$, $r' = 1.41$, hence bands like (11, 0, 12, 0) lying between $\lambda \lambda 2100-1975$ are strong.

No intercombination between the two systems of bands is known.

The energy values of the levels are given by

Band	Ionization potential (experimental)	Spectroscopic
X $^2\Pi_g$	12.5	12.2
a $^4\Pi_u$	16.1	16.1
A $^4\Pi_u$	—	16.7
b $^4\Pi_g$	—	18.2

Recently a set of absorption experiments has been carried out by Price and Collins (1935) which show that the photoelectric ionization of O₂ to O₂⁺ is effected in the same way as for N₂, i.e. there is no ionization by light of wave-length corresponding to the lowest ionization potential of 12.5 V which can ionize O₂ to the lowest state of O₂⁺ $^2\Pi_g$, but they obtain a set of absorption bands (H, I, ...) which can be formed into a Rydberg sequence coming to a limit at $130,800\text{ cm.}^{-1}$, i.e. 16.14 V. This is identified with the a $^4\Pi_u$ state. Another set of bands passes to a continuum at 18.2 V. This is identified with $^4\Sigma_g$. A third strong ionization continuum is found at 16.7 V round about $\lambda 740$, which is provisionally identified with the production of the state A $^2\Pi_u$. There appears to be no absorption corresponding to the first observed ionization potential, viz. 12.5 e-volts. Thus it appears that the photochemically active light which can ionize O₂ to O₂⁺ must have the energy equivalent to 16.20 e-volts at least, though the first ionization potential is 12.15 e-volts.

No negative bands of O₂⁺ have yet been detected in the spectrum of the night sky or the aurora. Also, no photochemical process has so far been found which can be interpreted as decomposing the oxygen molecule into atoms,

one of which is in the O^1S_0 state. In fact, our knowledge of the spectroscopy of O_2 and O_2^+ is meagre.

The value of the absorption coefficient at none of the supposed ionization continua has yet been obtained. It is stated by Price and Collins (1935) that a partial pressure of 0.01 mm. and a path of 1.5 m. (i.e. a path of 1.5 to 0.15 cm.) brings out the absorption quite clearly. According to Table I, we have this mass of oxygen at a height of about 100 km. It is therefore quite possible that the E layer ionization is produced by the ionization of O_2 to O_2^+ in the way supposed here.

The above summary of our knowledge of the spectra of O_2 and N_2 probably brings out clearly the necessity of undertaking a well-planned set of experiments on the spectroscopy of oxygen and nitrogen, particularly in the far ultra-violet, without which a satisfactory theory of the phenomena in the ionosphere, and of the luminous night-sky spectrum, is not possible.

Part of this work was done while the author was on tour in Europe and America as a Carnegie Fellow, and he wishes to acknowledge his indebtedness to the British Committee of the Carnegie Corporation for the award of the Carnegie grant to him. He also wishes to express his thanks to Professor E. A. Milne, F.R.S., and Professor H. H. Plaskett, F.R.S., for many useful discussions with them during his stay at Oxford. Thanks are also due to Professors H. Shapley and H. N. Russell, who were kind enough to discuss the contents of the paper with the author and offer many useful criticisms and suggestions.

SUMMARY

In this paper it is shown that a satisfactory theory of Upper Air Phenomena, such as the luminous night sky, the ionization in the different layers (E, F, . . .), etc., must be based on a precise knowledge of the action of ultra-violet sunlight (below $\lambda 3000$) on molecular oxygen and nitrogen. The knowledge which we possess at present is summarized in the present paper; and the nature of molecular ionization and excitation, and the heights at which they occur, are discussed in detail. It is shown that according to laboratory evidence available at present molecular ionization of O_2 and N_2 by photochemical action does not take place at the lowest ionization potential, but at the second ionization potential, i.e. the photon which causes ionization of O_2 and N_2 leaves the molecular ion excited. It is concluded that the knowledge we possess is rather scanty and does not enable us to start any adequate physical theory, beyond indicating barely the physical processes

which cause such phenomena. But the discussion brings out the necessity of carrying out well-planned laboratory experiments on the absorption spectra of O_2 and N_2 , without which it will not be possible to furnish an adequate explanation of upper air phenomena. The discussion also shows that the ultra-violet radiation from the sun differs widely from that of a black body, and in selected wave-lengths the sun must be emitting nearly a million times more photons than is given by a black body at $6500^\circ K$. This may possibly be due to the fact that the ultra-violet spectrum of the sun may consist of a continuous background of faint light on which are superposed emission lines of H, He, He^+ , Fe^+ , and other elements which are represented in the visible range by lines of subordinate series, or by patches of ultra-violet continuous light (near about $\lambda 500$) leaking through the solar atmosphere from a much hotter region inside the photosphere, as suggested by Professor H. N. Russell.

REFERENCES

- APPLETON, E. V. 1936 *Ann. Rep. Prog. Phys.* **2**, 129-165.
 APPLETON, E. V. and CHAPMAN, S. 1935 *Proc. Inst. Radio Engrs, N. Y.* **23**, 658.
 Brill, 1932 *Handb. Astrophys.* **5** (1), 128-209.
 CHAPMAN, S. 1930 *Mem. R. Met. Soc.* **3**, No. 26.
 1931 *Proc. Roy. Soc. A*, **132**, 353.
 DEJARDIN 1936 *Rev. Mod. Phys.* **8**, 1-30.
 FABRY and BUISSON 1913 *J. Phys. Radium*, **3**, 196.
 FOWLER and STRUTT 1917 *Proc. Roy. Soc. A*, **93**, 577.
 GÖTZ, MEETHAM and DOBSON 1934 *Proc. Roy. Soc. A*, **145**, 416.
 GURNEY 1928 *Mon. Not. R. Astr. Soc.* **88**, 377.
 HOPFIELD 1928 *Phys. Rev.* **31**, 1131.
 1930 *Phys. Rev.* **36**, 789.
 LADENBURG, R. W. 1935 *J. Opt. Soc. Amer.* **25**, 259.
 LYMAN 1928 "Ultra-violet Spectroscopy", p. 70.
 MARIS and HULBURT 1929 *Phys. Rev.* **33**, 412.
 MATHUR, L. S. and SENGUPTA, P. K. 1936 *Proc. Acad. Sci. U.P. Ind.* **5**, 187-226.
 MECKE 1927 *Z. Phys.* **42**, 390.
 MITRA and OTHERS 1936 *Proc. Nat. Inst. Sci. Ind.* **1**, 131-59.
 MULDER 1935 *Z. Astrophys.* **11**, 132.
 MÜLLIKEN 1933 *Phys. Rev.* **46**, 144.
 MULLIKEN and STEVENS 1933 *Phys. Rev.* **44**, 720.
 PETIT 1935 *Pub. Astr. Soc. Pacific*, **47**, 324.
 PRICE and COLLINS 1935 *Phys. Rev.* **48**, 714.
 REGENER 1934 *Phys. Z.* **35**, 788.
 SAHA 1935 *Proc. Nat. Inst. Sci.* **1**, 238.
 1936 *Science and Culture*, **1**, 476.
 SLIPHER 1933 *Mon. Not. R. Astr. Soc.* **93**, 657.
 SLIPHER and SOMMER 1929 *Naturwissenschaften*, **17**, 802.
 SPONER 1933 "Molekülspektoren", p. 17.
 STORMER 1931 *Ergebn. kosm. Phys.* **1**, 1-82.
 TATE and SMITH 1932 *Phys. Rev.* **39**, 270.

69. ON THE PROPAGATION OF ELECTRO-MAGNETIC WAVES THROUGH THE EARTH'S ATMOSPHERE

(PAPER I)

M. N. SAHA, R. N. RAI AND K. B. MATHUR

(*Proc. Nat. Inst. Sci. Ind.*, **4**, 53, 1938)

(*Read November 6, 1937.*)

INTRODUCTION

The introduction to this paper has already been given in another with the same heading published in these *Proceedings* (Vol. III, p. 359, 1937) henceforth called paper 2. The present paper deals with the derivation of the equations given in §2, pp. 363 and 364 of paper 2. There only a bare statement of the equations was given; here the exact procedure of their derivation is given. The programme of these series of papers may be defined as the wave-treatment of the problem of propagation dealing with questions of polarization, reflection, oblique propagation, and absorption of the waves. We first give a fuller description of the notation employed.

NOTATION.

The notation used in this field of investigation differs so widely from one author to another that the reading of papers by different authors is attended with a certain amount of difficulty. It is desirable that a system of international notations be agreed upon. In this paper, an attempt has been made to use a system of symbols which may be acceptable to the different schools of investigators. We have, as far as possible, adhered to the symbols used by S. K. Mitra, which were mostly adopted from the writings of Appleton and his school. In some points we have found it necessary to deviate from Mitra's symbols. An explanation of the system of symbols is therefore given at the beginning.

E	.. Electric Field Intensity with components	E_x, E_y, E_z .
D	.. Electric Displacement Vector	.. D_x, D_y, D_z .
H	.. Magnetic Field Vector	.. H_x, H_y, H_z .
B	.. Magnetic Polarization	
P	.. Polarization	.. P_x, P_y, P_z .
h	.. Earth's magnetic field components	.. h_x, h_y, h_z .

(Mitra has used H for this quantity. But it produces a certain amount of confusion with the magnetic field vector, hence we have used ' h ' to denote the earth's field.)

p_h	.. Larmor Frequency	$\frac{eh}{mc}$.
p_x, p_y, p_z	.. Components of Larmor Frequency.	
p	.. Pulsatance of the electromagnetic wave.	
N	.. Number of electrons, or ions per c.c. at any height. Whenever necessary the subscript 'e' for electron, 'i' for ion is affixed to N . Thus N_e denotes number of electrons. But usually the suffix is not used.	
ω^2	$= p \frac{4\pi N e^2}{m}$	either for electrons or ions.
ν	.. collisional frequency, i.e., number of collisions made by an ion or electron in unit time.	

$$\begin{aligned}
 (\omega_x, \omega_y, \omega_z) &= \frac{1}{p} (p_x, p_y, p_z), \omega \text{ is the resultant value of} \\
 &(\omega_x, \omega_y, \omega_z) \\
 &= \frac{1}{p} (p_h) = \frac{eh}{mcp}. \\
 r &= \frac{p_0^2}{p^2} = \frac{4\pi N e^2}{mp^2}. \\
 \beta &= 1 - \frac{i\nu}{p} = 1 - i\delta. \\
 q &= \text{Complex Refractive Index.} \\
 &= \mu - i\chi.
 \end{aligned}$$

§ 1.

THE FUNDAMENTAL EQUATIONS.

The fundamental equations for the propagation of electromagnetic waves are:—

$$\left. \begin{aligned}
 \text{Curl } H &= \frac{1}{c} \dot{D} \\
 \text{Curl } E &= -\frac{1}{c} \dot{B} \\
 \text{Div } D &= 4\pi p \\
 \text{Div } B &= 0 \\
 D &= kE = E + 4\pi P
 \end{aligned} \right\} \quad \dots (1.1)$$

For the present case, we take $\mu=1$ so that

$$B=\mu H=H.$$

From equation (1.1) it can be deduced in the usual way that

$$\left. \begin{aligned} \nabla^2 H &= \frac{1}{c^2} \ddot{H} - \frac{4\pi}{c} \text{Curl } \dot{P} \\ \text{and} \quad \nabla^2 E &= \frac{1}{c^2} \ddot{E} + \frac{4\pi}{c^2} \ddot{P} - 4\pi \text{grad div } P \end{aligned} \right\} \dots (1.2)$$

We have now to express P in terms of E .

Let us suppose that on account of the e.m. field of the radio wave the charged particles suffer the displacement ξ, η, ζ . The equations of motion of the charged particles are given by

$$\left. \begin{aligned} m\ddot{\xi} &= eE_x - g\dot{\xi} + \frac{e}{c}(\dot{\eta}h_x - \dot{\zeta}h_y) + aP_x \\ m\ddot{\eta} &= eE_y - g\dot{\eta} + \frac{e}{c}(\dot{\xi}h_x - \dot{\zeta}h_z) + aP_y \\ m\ddot{\zeta} &= eE_z - g\dot{\zeta} + \frac{e}{c}(\dot{\xi}h_y - \dot{\eta}h_x) + aP_z \end{aligned} \right\} \dots (1.3)$$

Here $-g(\dot{\xi}, \dot{\eta}, \dot{\zeta})$ represents the frictional force due to collisions.

The third term $\dots \frac{e}{c}(v \times h)$ represents the deflecting force due to the earth's magnetic field.

We have further $P = Ne(\xi, \eta, \zeta)$, where N is the number of electrically charged particles per unit volume.

The last term in (1.3) represents the action of the polarization forces. It is now usual to take $a=0$.

We shall replace (ξ, η, ζ) by $\frac{1}{Ne}(P_x, P_y, P_z)$ throughout (1.3), and let us further suppose that P is proportional to e^{ipt} . Then the equations (1.3) reduce to

$$-\frac{mp^2}{Ne}P_x = eE_x - \frac{igp}{Ne}P_x + \frac{ip}{Ne}(P \times h)_x$$

and two other similar equations.

The form of the equations can be much simplified if we make the following substitutions:—

$$\left. \begin{aligned} -\frac{mp^2}{Ne^2} &= -\frac{4\pi p^2}{p_0^2} = -\frac{4\pi}{r} \\ \frac{gp}{Ne^2} &= \frac{g}{m} \frac{p}{Ne^2/m} = \frac{4\pi}{r} \frac{v}{p} \\ \frac{ph}{eNe} &= \frac{eh}{mc} \frac{4\pi p}{4\pi Ne^2/m} = \frac{4\pi p p_h}{p_0^2} = \frac{4\pi \omega}{r} \end{aligned} \right\} \dots (1.4)$$

Then the equations take the form

$$\left. \begin{aligned} \beta P_x + i\omega_z P_y - i\omega_y P_z &= -\frac{r}{4\pi} E_x \\ -i\omega_z P_x + \beta P_y + i\omega_x P_z &= -\frac{r}{4\pi} E_y \\ i\omega_y P_x - i\omega_x P_y + \beta P_z &= -\frac{r}{4\pi} E_z \end{aligned} \right\} \dots (1.5)$$

These equations can be easily solved by the usual algebraic methods. We can put

$$\left. \begin{aligned} \frac{P_x}{A} &= \Delta_{11}E_x + \Delta_{21}E_y + \Delta_{31}E_z \\ \frac{P_y}{A} &= \Delta_{12}E_x + \Delta_{22}E_y + \Delta_{32}E_z \\ \frac{P_z}{A} &= \Delta_{13}E_x + \Delta_{23}E_y + \Delta_{33}E_z \end{aligned} \right\} \dots (1.6)$$

$$\text{where } A = \frac{r}{4\pi\beta} \frac{1}{\beta^2 - \omega^2}.$$

Δ_{rs} , etc. are the subdeterminants of the determinant formed by the coefficients of the quantities P_x, P_y, P_z in equations (1.5).

It can be easily shown that

$$\left. \begin{aligned} \Delta_{11} &= \omega_x^2 - \beta^2 & \Delta_{21} &= \omega_x \omega_y + i\beta \omega_z & \Delta_{12} &= \omega_x \omega_y - i\beta \omega_z \\ \Delta_{22} &= \omega_y^2 - \beta^2 & \Delta_{32} &= \omega_z \omega_y + i\beta \omega_x & \Delta_{23} &= \omega_z \omega_y - i\beta \omega_x \\ \Delta_{33} &= \omega_z^2 - \beta^2 & \Delta_{13} &= \omega_x \omega_z + i\beta \omega_y & \Delta_{31} &= \omega_x \omega_z - i\beta \omega_y \end{aligned} \right\} (1.7)$$

These results will be utilized later.

§ 2.

PROPAGATION ALONG THE z-AXIS.

We shall first consider the propagation of the rays along the z-axis. Then the second set of equations (1.2) reduces to the three equations:—

$$\left. \begin{aligned} \frac{d^2 E_x}{dz^2} - \frac{1}{c^2} \frac{d^2 E_x}{dt^2} &= \frac{4\pi}{c^2} \frac{d^2 P_x}{dt^2} \\ \frac{d^2 E_y}{dz^2} - \frac{1}{c^2} \frac{d^2 E_y}{dt^2} &= \frac{4\pi}{c^2} \frac{d^2 P_y}{dt^2} \\ \frac{d^2 E_z}{dz^2} - \frac{1}{c^2} \frac{d^2 E_z}{dt^2} &= \frac{4\pi}{c^2} \frac{d^2 P_z}{dt^2} - 4\pi \frac{d^2 P_z}{dz^2} \end{aligned} \right\} \dots (2.1)$$

for the terms arising out of $\text{Grad Div } P$ are now simplified as

$$\frac{\partial}{\partial x}(\text{Div } P) = 0, \quad \frac{\partial}{\partial y}(\text{Div } P) = 0 \quad \text{and} \quad \frac{\partial}{\partial z}(\text{Div } P) = \frac{d^2 P_z}{dz^2}$$

Further ∇^2 reduces to $\frac{d^2}{dz^2}$.

The third of equations (2.1) is

$$\left(\frac{d^2}{dz^2} - \frac{1}{c^2} \frac{d^2}{dt^2} \right) (E_z + 4\pi P_z) = 0. \quad \dots (2.2)$$

Now from the condition $\text{Div } D = 0$, we have

$$\frac{\partial}{\partial z} [E_z + 4\pi P_z] = 0. \quad \dots (2.3)$$

From (2.2) and (2.3), we have

$$D_z = E_z + 4\pi P_z = 0. \quad \dots (2.4)$$

As according to (1.6), P_z is a linear function of E_x, E_y, E_z , equation (2.4) enables us to express E_z in terms of E_x and E_y . We have

$$E_z + 4\pi A (\Delta_{13}E_x + \Delta_{23}E_y + \Delta_{33}E_z) = 0.$$

$$E_z = -\frac{\Delta_{13}E_x + \Delta_{23}E_y}{\left(\Delta_{33} + \frac{1}{4\pi A}\right)}, \quad \dots \quad (2.5)$$

The equations (2.1) can now be put in the form:—

$$\left. \begin{aligned} \frac{d^2 E_x}{dz^2} &= \frac{K_{11}}{c^2} \frac{d^2 E_x}{dt^2} + \frac{K_{12}}{c^2} \frac{d^2 E_y}{dt^2} \\ \frac{d^2 E_y}{dz^2} &= \frac{K_{21}}{c^2} \frac{d^2 E_x}{dt^2} + \frac{K_{22}}{c^2} \frac{d^2 E_y}{dt^2} \end{aligned} \right\}, \quad \dots \quad (2.6)$$

where

$$\begin{aligned} K_{11} &= 1 + 4\pi A \left\{ \Delta_{11} - \frac{\Delta_{13}\Delta_{31}}{\Delta_{33} + \frac{1}{4\pi A}} \right\}, \\ K_{12} &= 4\pi A \left\{ \Delta_{21} - \frac{\Delta_{31}\Delta_{23}}{\Delta_{33} + \frac{1}{4\pi A}} \right\}, \\ K_{21} &= 4\pi A \left\{ \Delta_{12} - \frac{\Delta_{32}\Delta_{13}}{\Delta_{33} + \frac{1}{4\pi A}} \right\}, \\ K_{22} &= 1 + 4\pi A \left\{ \Delta_{22} - \frac{\Delta_{23}\Delta_{32}}{\Delta_{33} + \frac{1}{4\pi A}} \right\}. \quad \dots \quad (2.7) \end{aligned}$$

It is easily seen that

$$\begin{aligned} D_x &= K_{11}E_x + K_{12}E_y \\ D_y &= K_{21}E_x + K_{22}E_y \end{aligned} \quad \dots \quad (2.8)$$

Equations for the propagation of the magnetic vector.

Instead of taking (1.2) we take the equation (1.1). We have then

$$\nabla^2 H = -\frac{1}{c} \text{curl } \dot{D} \quad \dots \quad (2.9)$$

$$\left(\text{for curl curl } H = -\nabla^2 H = \frac{1}{c} \text{curl } \dot{D} \right),$$

These equations reduce to

$$\frac{d^2 H_x}{dz^2} = \frac{1}{c} \frac{d\dot{D}_y}{dz}, \quad \frac{d^2 H_y}{dz^2} = -\frac{1}{c} \frac{d\dot{D}_x}{dz}. \quad \dots \quad (2.10)$$

Now from (2.8) we have

$$\begin{aligned} \dot{D}_x &= K_{11}\dot{E}_x + K_{12}\dot{E}_y \\ \dot{D}_y &= K_{21}\dot{E}_x + K_{22}\dot{E}_y \end{aligned} \quad \dots \quad (2.11)$$

since the quantities K are not functions of time.

Further from the second equation of (1.1), we have

$$\text{curl } E = \left(-\frac{dE_y}{dz}, \frac{dE_x}{dz}, 0 \right) = -\frac{1}{c} \left(\frac{dH_x}{dt}, \frac{dH_y}{dt}, 0 \right). \quad (2.12)$$

Applying these conditions to (2.10) and (2.11) we have, when the quantities K do not vary with z ,

$$\left. \begin{aligned} \frac{d^2 H_x}{dz^2} &= \frac{K_{22}}{c^2} \frac{d^2 H_x}{dt^2} - \frac{K_{21}}{c^2} \frac{d^2 H_y}{dt^2} \\ \frac{d^2 H_y}{dz^2} &= -\frac{K_{12}}{c^2} \frac{d^2 H_x}{dt^2} + \frac{K_{11}}{c^2} \frac{d^2 H_y}{dt^2} \end{aligned} \right\}. \quad \dots \quad (2.13)$$

Also from (2.12) and the first equation of (1.1) we have, utilizing (2.8),

$$\left. \begin{aligned} \frac{dE_x}{dz} &= -\frac{1}{c} \frac{dH_y}{dt}, \quad \frac{dE_y}{dz} = \frac{1}{c} \frac{dH_x}{dt} \\ \frac{dH_x}{dz} &= \frac{K_{21}}{c} \frac{dE_x}{dt} + \frac{K_{22}}{c} \frac{dE_y}{dt} \\ \frac{dH_y}{dz} &= -\frac{K_{11}}{c} \frac{dE_x}{dt} - \frac{K_{12}}{c} \frac{dE_y}{dt} \end{aligned} \right\}, \quad \dots \quad (2.14)$$

when $p_y=0$, the last two reduces to

$$\left. \begin{aligned} \frac{dH_x}{dz} &= \frac{iL}{c} \frac{dE_x}{dt} + \frac{K_{22}}{c} \frac{dE_y}{dt}, \\ \frac{dH_y}{dz} &= -\frac{K_{11}}{c} \frac{dE_x}{dt} + \frac{iL}{c} \frac{dE_y}{dt}, \end{aligned} \right\} \quad \dots \quad (2.14')$$

where

$$L = -r(\beta - r)\omega_z/C.$$

We can now calculate the quantities K from the relations (2.7). First let us suppose that the collision frequency ν can be neglected. We have then

$$4\pi A = \frac{r}{1 - \omega^2},$$

$$\Delta_{33} + \frac{1}{4\pi A} = \frac{\{(1 - \omega^2) - r(1 - \omega_z^2)\}}{r} = \frac{C}{r},$$

where

$$C = 1 - \omega^2 - r(1 - \omega_z^2).$$

$$\left. \begin{aligned} \Delta_{11} - \frac{\Delta_{13}\Delta_{31}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{(1 - \omega^2)(r + \omega_x^2 - 1)}{C} \\ \Delta_{22} - \frac{\Delta_{23}\Delta_{32}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{(1 - \omega^2)(r + \omega_y^2 - 1)}{C} \\ \Delta_{21} - \frac{\Delta_{31}\Delta_{23}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{(1 - \omega^2)\{\omega_x\omega_y + i\omega_z(1 - r)\}}{C} \\ \Delta_{12} - \frac{\Delta_{13}\Delta_{32}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{(1 - \omega^2)\{\omega_x\omega_y - i\omega_z(1 - r)\}}{C} \end{aligned} \right\}. \quad (2.15)$$

From these expressions, we obtain the following values for the K 's.

$$\left. \begin{aligned} K_{11} &= 1 + r \frac{\omega_x^2 - 1 + r}{C} \\ K_{22} &= 1 + r \frac{\omega_y^2 - 1 + r}{C} \\ K_{12} &= r \frac{\omega_x\omega_y + i(1 - r)\omega_z}{C} \\ K_{21} &= r \frac{\omega_x\omega_y - i(1 - r)\omega_z}{C} \end{aligned} \right\}. \quad \dots \quad (2.16)$$

The expressions are considerably simplified if we put $p_y = \omega_y = 0$. This means that we are taking the magnetic meridian as our $(x-z)$ -plane.

We have now

$$\left. \begin{aligned} K_{11} &= 1 + r \frac{\omega_x^2 - 1 + r}{C} = \frac{(1-r)(1-r-\omega^2)}{C} \\ K_{22} &= 1 + r \frac{r-1}{C} \\ K_{12} &= -K_{21} = -iL \text{ where } L = -\frac{r(1-r)\omega_x}{C} \end{aligned} \right\} \quad (2.17)$$

When collisions are taken into account, it can be proved after some work that we have now the following relations:

$$\Delta_{33} + \frac{1}{4\pi A} = \frac{1}{r} \{ \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega_x^2) \} = \frac{C'}{r},$$

where $C' = \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega_x^2) \quad \dots (2.18)$

$$\left. \begin{aligned} \Delta_{11} - \frac{\Delta_{13}\Delta_{31}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{\beta(\beta^2 - \omega^2) \{ r\beta + \omega_x^2 - \beta^2 \}}{C'} \\ \Delta_{22} - \frac{\Delta_{23}\Delta_{32}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{\beta(\beta^2 - \omega^2) (r\beta + \omega_y^2 - \beta^2)}{C'} \\ \Delta_{21} - \frac{\Delta_{31}\Delta_{23}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{\beta(\beta^2 - \omega^2) \{ \omega_x\omega_y + i\omega_x(\beta - r) \}}{C'} \\ \Delta_{12} - \frac{\Delta_{13}\Delta_{32}}{\Delta_{33} + \frac{1}{4\pi A}} &= \frac{\beta(\beta^2 - \omega^2) \{ \omega_x\omega_y - i\omega_x(\beta - r) \}}{C'} \end{aligned} \right\} \quad (2.19)$$

It is easy to see that the relations (2.15) are deducible from (2.19) when collisions are neglected, i.e. $\beta = 1$.

We can now write out values of K 's from the above relations. We have

$$\left. \begin{aligned} K_{11} &= 1 - r \frac{\beta^2 - r\beta - \omega_x^2}{C'} \\ K_{22} &= 1 - r \frac{\beta^2 - r\beta - \omega_y^2}{C'} \\ K_{12} &= \frac{r\{\omega_x\omega_y + i\omega_x(\beta - r)\}}{C'} \\ K_{21} &= \frac{r\{\omega_x\omega_y - i\omega_x(\beta - r)\}}{C'} \end{aligned} \right\} \quad \dots \quad (2.20)$$

Considerable simplification is introduced by putting $p_y = \omega_y = 0$. We have now

$$\left. \begin{aligned} K_{11} &= 1 - r \frac{\beta^2 - r\beta - \omega_x^2}{C'} = \frac{(r-\beta)(\omega^2 + r\beta - \beta^2)}{C'} \\ K_{22} &= 1 - r \frac{\beta^2 - r\beta}{C'} \\ -K_{12} &= K_{21} = iL, \\ \text{where } L &= -r(\beta - r)\omega_x/C'. \end{aligned} \right\} \quad (2.21)$$

When $\beta = 1$ (no collision), these expressions reduce to (2.17).

§ 3. SOLUTION OF THE FUNDAMENTAL EQUATIONS

The rigorous solution of the fundamental equations presents great difficulty, since the quantity $p_0^2 = \frac{4\pi N e^2}{m}$ is not a constant, but varies with height. Let us first treat p_0^2 as a constant, and see what result is obtained.

Let us put

$$(E_x, E_y, H_x, H_y) = (A_1, B_1, C_1, D_1) e^{i\phi} \quad \dots (3.1)$$

where $\phi = p \left(t \mp \frac{\mu z}{c} \right)$; the minus sign holds for the outgoing wave, the plus sign for the reflected wave. ' μ ' is the refractive index, which we have to find out. When we substitute (3.1) in (2.14) for the outgoing wave, we have the following relation amongst the constants A_1, B_1, C_1, D_1 :

$$\left. \begin{aligned} \mu A_1 &= D_1, \mu B_1 = -C_1 \\ \mu C_1 &= -iL A_1 - K_{22} B_1, \mu D_1 = K_{11} A_1 - iL B_1 \end{aligned} \right\} \quad (3.2)$$

From these equations, or directly from (2.14), we obtain

$$\left. \begin{aligned} (\mu^2 - K_{11}) A_1 + iL B_1 &= 0 \\ -iL A_1 + (\mu^2 - K_{22}) B_1 &= 0 \end{aligned} \right\}, \quad \dots \quad (3.3)$$

or for the magnetic vectors

$$\left. \begin{aligned} (\mu^2 - K_{11}) D_1 + iL C_1 &= 0 \\ -iL D_1 + (\mu^2 - K_{22}) C_1 &= 0 \end{aligned} \right\}, \quad \dots \quad (3.3')$$

i.e. μ^2 is given by the roots of the quadratic equation

$$(\mu^2 - K_{11})(\mu^2 - K_{22}) - L^2 = 0. \quad \dots (3.4)$$

Let us put

$$\frac{K_{11} - K_{22}}{2L} = f.$$

Then it can be easily shown after a little work that the two values of μ are given by

$$\left. \begin{aligned} \mu_1^2 &= K_{11} - Lf(1 - \sqrt{1 + L/f^2}) = K_{11} - L\rho_1 \\ \mu_2^2 &= K_{11} - Lf(1 + \sqrt{1 + L/f^2}) = K_{11} - L\rho_2 \end{aligned} \right\} \quad (3.5)$$

where

$$\rho_1 = f(1 - \sqrt{1 + L/f^2}), \rho_2 = f(1 + \sqrt{1 + L/f^2}). \quad (3.6)$$

ρ_1 and ρ_2 are the roots of the equation,

$$\rho^2 - \frac{K_{11} - K_{22}}{L} \rho - 1 = 0.$$

From equations (3.3) and (3.5) we have

$$\frac{B_1}{A_1} = \frac{\mu^2 - K_{11}}{-iL} = -i\rho,$$

or $B_1 = -i\rho A_1, C_1 = i\rho \mu A_1, D_1 = \mu A_1$.

Hence we have from (3.1),

$$\left. \begin{aligned} E_x &= A_1 \cos \phi, E_y = A_1 \rho \sin \phi \\ H_x &= -\mu A_1 \rho \sin \phi, H_y = \mu A_1 \cos \phi \end{aligned} \right\} \quad \dots (3.7)$$

These equations show that the two waves are elliptically polarized. We have

$$\left. \begin{aligned} E_x^2 + \frac{E_y^2}{\rho^2} &= A_1^2 \\ \frac{H_x^2}{\rho^2} + H_y^2 &= \mu^2 A_1^2 \end{aligned} \right\} \dots \dots (3.8)$$

The ratio of the axes of the ellipses are—

(a) for the electric vector x -axis : y -axis = $1 : \rho$

(b) for the magnetic vector x -axis : y -axis = $\rho : 1$.

The sense of rotation is given by equations (3.7) and the sign of ρ can be taken only after we have discussed the values of ρ_1 and ρ_2 .

Let us now find out the special characteristics of the two waves. It is necessary now that the signs be properly taken.

In the northern hemisphere, the northseeking (positive) magnetic pole points downwards as shown in the figure. Let 'h' denote the absolute value of the magnetic field. Then if ' δ ' be the dip-angle, we have

$$h_x = h \cos \delta, h_z = -h \sin \delta.$$

Now $\frac{eh}{mcp} = \omega$ is itself negative, because 'e' is negative.

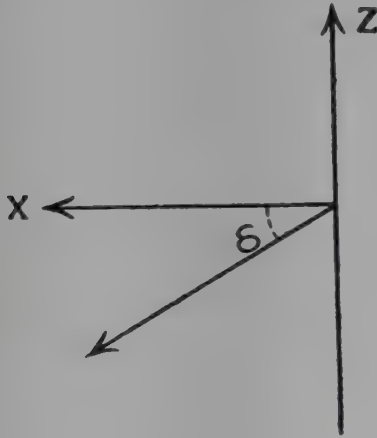


Fig. 1

We have therefore

$$\omega_x = -w \cos \delta, \omega_z = w \sin \delta,$$

where w is the quantity $\left| \frac{eh}{mcp} \right|$.

In the southern hemisphere, the dip is upwards for the positive pole, hence we have simply to substitute $(-\delta)$ for δ in the above expression. With the notation used here it is easy to see that

$$\left. \begin{aligned} K_{11} &= \frac{(1-r)(1-r-\omega^2)}{C} = \frac{t(t+\omega^2)}{C}, t=r-1 \\ L &= -\frac{r(1-r)\omega_z}{C} = \frac{t(1+t)\omega \sin \delta}{C} \\ f &= \frac{K_{11}-K_{22}}{2L} = \frac{w \cos^2 \delta}{2t \sin \delta} \end{aligned} \right\} (3.9)$$

We have now

$$\left. \begin{aligned} \mu_1^2 &= K_{11} - L\rho_1 = K_{11} - Lf(1 - \sqrt{1+1/f^2}) \\ C\mu_1^2 &= t(t+\omega^2) - \frac{(1+t)}{2} \omega^2 \cos^2 \delta \left\{ 1 - \sqrt{\frac{1+4t^2 \sin^2 \delta}{\omega^2 \cos^4 \delta}} \right\} \\ C\mu_2^2 &= t(t+\omega^2) - \frac{(1+t)}{2} \omega^2 \cos^2 \delta \left\{ 1 + \sqrt{\frac{1+4t^2 \sin^2 \delta}{\omega^2 \cos^4 \delta}} \right\} \end{aligned} \right\} (3.10)$$

The expressions for μ_1^2 , μ_2^2 are independent of the sign of ' δ ' and hence hold for both hemispheres. We further observe that

(a) $\mu_1^2 = 0$ when $t=0$.

Hence μ_1 represents the conventional ordinary wave, for $t=0$ is equivalent to the condition $p_0^2 = p^2$. (3.11)

(b) To prove that $\mu_2^2 = 0$ when $t^2 = \omega^2$.

In this case, we have

$$\sqrt{1 + \frac{4t^2 \sin^2 \delta}{\omega^2 \cos^4 \delta}} = 1 + \frac{2 \sin^2 \delta}{\cos^2 \delta}.$$

$$\therefore 1 + \sqrt{1+1/f^2} = 2 \sec^2 \delta, \text{ and}$$

$$\begin{aligned} C\mu_2^2 &= t(t+\omega^2) - (1+t)\omega^2 \\ &= t^2 - \omega^2 \\ &= 0. \end{aligned}$$

This condition gives us that $\mu_2 = 0$ when $t = \pm \omega$,

$$\text{or } \frac{p_0^2}{p^2} = 1 \pm \frac{p_h}{p} \text{ or } p_0^2 = p^2 \pm p p_h. \quad (3.12)$$

These are the conditions of reflection for the extraordinary wave. μ_2 therefore represents the extraordinary wave.

Limiting cases:—

(1) When $\delta=0$ (Magnetic Equator—Transverse Case).

We can show from (3.10) that

$$\mu_1^2 = -t = 1-r, \mu_2^2 = -\frac{t^2 - \omega^2}{t + \omega^2}.$$

The $(\mu_1^2, 1-r)$ curve is the straight line representing the ordinary wave in Mitra's Report (1935). The μ_2^2, r curve resolves into two curves on either side of the $(\mu_1^2, 1-r)$ line.

(2) When $\delta = \pm \frac{\pi}{2}$ (Magnetic Poles—Longitudinal case).

Now $\cos \delta=0$, $\sin \delta = \pm 1$, and we easily see from (3.10) that

$$\begin{aligned} \mu_1^2 &= \frac{t+\omega}{\omega-1}, & \mu_2^2 &= \frac{\omega-t}{1+\omega}, \\ &= \frac{1-r-\omega}{1-\omega}, & &= \frac{\omega+1-r}{\omega+1}, \\ &= 1 - \frac{r}{1-\omega}, & &= 1 - \frac{r}{1+\omega}. \end{aligned}$$

So the (μ_1^2, r) (μ_2^2, r) curves reduce to straight lines, which are reproduced in Mitra's Report, p. 142.

§ 4. POLARIZATION

As mentioned in §3, the polarization factors are given by

$$\rho_1 = f[1 - \sqrt{1 + 1/f^2}], \quad \rho_2 = f[1 + \sqrt{1 + 1/f^2}], \quad (4.1)$$

since $f = \frac{\omega^2 \cos^2 \delta}{2t \sin \delta}$ and $t = r - 1$, $r = \frac{p_0^2}{p^2}$, f varies with the height of the point at which the wave is being considered, t varies from -1 at the ground to zero at $r=1$. We need consider only the polarization of the ground wave. We have then

$$t = -1, \\ f = -\frac{\omega \cos^2 \delta}{2 \sin \delta}. \quad \dots \quad (4.2)$$

For the o-wave.

(a) Northern hemisphere

$$\rho_1 = -\frac{\omega \cos^2 \delta}{2 \sin \delta} \left[1 - \sqrt{1 + \frac{4 \sin^2 \delta}{\omega^2 \cos^4 \delta}} \right]. \quad \dots \quad (4.3)$$

Southern hemisphere, now ' δ ' must be changed to ' $-\delta$ '; we have then

$$\rho_1 = \frac{\omega \cos^2 \delta}{2 \sin \delta} \left[1 - \sqrt{1 + \frac{4 \sin^2 \delta}{\omega^2 \cos^4 \delta}} \right]. \quad \dots \quad (4.4)$$

For the x-wave.

(b) Northern hemisphere

$$\rho_2 = -\frac{\omega \cos^2 \delta}{2 \sin \delta} \left[1 + \sqrt{1 + \frac{4 \sin^2 \delta}{\omega^2 \cos^4 \delta}} \right]. \quad \dots \quad (4.5)$$

Southern hemisphere

$$\rho_2 = \frac{\omega \cos^2 \delta}{2 \sin \delta} \left[1 + \sqrt{1 + \frac{4 \sin^2 \delta}{\omega^2 \cos^4 \delta}} \right]. \quad \dots \quad (4.6)$$

In the table given below, we have calculated values of ρ_1 , ρ_2 for a number of selected stations, for $\lambda=100$ meters. They are also given under fig. 2.

TABLE I

Place	δ	h	$r = \frac{eh}{mc\beta}$	$f = \frac{r \cos^2 \delta}{2 \sin \delta}$	Ordinary ρ_1	Extra-ordinary ρ_2	Remarks
N. Pole ..	90°	..	..	..	1	-1	
Lerwick	72° 42'	4884	4509	-0208	9794	-1.0210	
Slough	66° 54'	4702	4419	-0370	9633	-1.0373	
Allahabad	46°	5182	487	-1653	8487	-1.1793	
Bombay	25° 30'	4135	3710	-3613	7017	-1.4213	
Huancayo	2° 3'	2963	2693	-3.757	129	-7.643	
North of Equator ..	0	..	..	$-\infty$	0	$-\infty$	
South of Equator ..	0	..	..	$+\infty$	0	$+\infty$	
La Quiaca	-12° 21'	2684	2523	5631	-5849	1.711	
Pilar	-25° 55'	2732	2576	2387	-7896	1.267	
Batavia	-32° 26'	4369	4121	2752	-7619	1.312	
Watheroo	-64° 19'	2757	259	0271	-9732	1.0274	
Melbourne	..	..	..	..	-9569	1.0451	
S. Pole	-90°	..	..	..	-1	1	

EXPERIMENTAL CONFIRMATION

These results have been experimentally confirmed. Berkner states that at Huancayo: The ordinary ray is

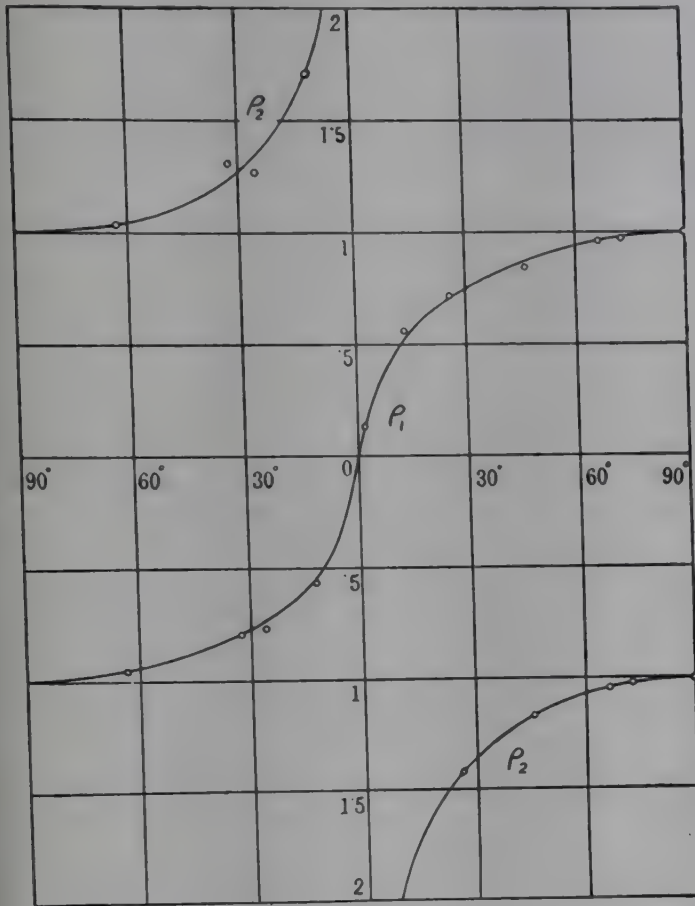


Fig. 2

polarized with its electric vector along the magnetic north-south. Table (1) shows that

$$E_x\text{-axis} : E_y\text{-axis} = 1 : 1.29$$

i.e. the electric vector is mainly along the x -axis, i.e. magnetic north-south.

The extraordinary ray is polarized with its electric vector along the magnetic east-west. Table (1) shows that

$$E_x\text{-axis} : E_y\text{-axis} = 1 : 7.643.$$

The variation of polarization for the o - and x -waves with latitude are shown in fig. 2.

CONCLUSION

It is shown that if the complex refractive index be regarded as constant we get the same conditions for reflection and polarization of the radio-waves for vertical propagation as was obtained by Appleton. But the refractive indices vary with height, hence the treatment given here should be replaced by a wave-treatment. A simple case of wave-treatment has already been published in paper 2.

REFERENCES

- ¹ M. N. SAHA and R. N. RAI—*Proc. Nat. Inst. Sci. India*, Vol. 3, pp. 359–369, (1937). (Paper 2).
- ² S. K. MITRA. (Report 1.)—*Proc. Nat. Inst. Sci. India*, Vol. 1, pp. 131–215, (1935).
- ³ BERKNER and WELLS.—*Terr. Mag.*, Vol. 42, p. 73, (1937).

70. ON THE IONIZATION OF THE UPPER ATMOSPHERE

M. N. SAHA AND R. N. RAI

(*Proc. Nat. Inst. Sci. Ind.*, **4**, 319, 1938)

(Received April 25, 1938)

1. INTRODUCTION

There are at present two works attempting a theoretical explanation of the ionization of the Upper Atmosphere. First, the work of A. Pannekoek (1926), which is thermodynamical, and is based upon Saha's theory of thermal ionization of atoms as extended by Milne (1924) and Woltjer (1925) to material systems traversed by radiation from an external body at a higher temperature. The second method is that of S. Chapman (1931 *a, b*) who considers

the ionization produced by the absorption of a monochromatic beam of light in an atmosphere in which the density is assumed to vary exponentially. Prof. Chapman in a Bakerian lecture in 1931 gave accounts of both theories side by side, but he does not appear to have tried to demonstrate the connection between the two methods of calculating the ionization of the upper atmosphere. It will be shown presently that the two theories are not

really different; when Chapman's theory is properly developed and extended, it leads to the same result as that of Pannekoek.

2. PANNEKOEK'S WORK

It is necessary to start with a critical description of the main results of these two theories. Pannekoek (1926) shows that the number of electrons produced by the ionization of any one of the constituents in the earth's atmosphere can be obtained from the formula

$$K = \frac{n_+ n_e}{N} = \left(\frac{n_+ n_e}{N} \right)_0 \frac{\int_{\nu_0}^{\infty} \psi(\nu) \cdot I(\nu) \cdot d\nu}{\int_{\nu_0}^{\infty} \psi(\nu) \cdot e^{-\frac{h\nu}{kT}} \left\{ \frac{8\pi h\nu^3}{c^2} + I(\nu) \right\} \cdot d\nu}, \quad (1)$$

where

$\left(\frac{n_+ n_e}{N} \right)_0 = K_0 =$ Reaction isochore under equilibrium conditions,

N = the number of atoms per unit volume,

n_+ = the number of ions per unit volume,

n_e = the number of electrons per unit volume,

$I(\nu)$ = the intensity of radiation of frequency ν .

$\psi(\nu)$ denotes the probability of ionization by light of unit intensity. $\psi(\nu)$ is connected with the atomic absorption coefficient $\tau(\nu)$ by the relation

$$\psi(\nu) = \tau(\nu)/h\nu.$$

There are two things to be noticed about this formula. First, that ionization starts at a frequency ν_0 and is produced by radiation of higher frequency just as we know from laboratory experiments. Secondly that the values of the density of electrons or of positive ions which we obtain from the above formula are *equilibrium values*, i.e. they are the values of concentration when a condition of equilibrium has been established between the rate of ionization due to solar radiation and the rate of disappearance due to recombination or any other process.

3. CHAPMAN'S WORK

Chapman (1931a) shows, following an earlier work by Lenard (1911), that a monochromatic beam of radiation, of intensity $I(\nu)_0$ just outside the earth's atmosphere, is reduced in its passage through the earth's atmosphere, at a slanting angle χ , to the intensity $I(\nu)$ given by the formula

$$I(\nu) = I(\nu)_0 \text{Exp} \left\{ -A(\nu) \cdot \rho_0 \cdot H \cdot \sec \chi \cdot e^{-\frac{z}{H}} \right\}. \quad (2)$$

Here $A(\nu)$ is the mass absorption coefficient, and $H = kT/Mg$ is the height of the homogeneous atmosphere. The temperature is assumed to be constant.

Then we have

$$\frac{dI(\nu)}{dz} = I(\nu)_0 \cdot A(\nu) \cdot \rho_0 \cdot \sec \chi \cdot \text{Exp} \left\{ -\frac{z}{H} - A(\nu) \cdot \rho_0 \cdot H \cdot \sec \chi \cdot e^{-\frac{z}{H}} \right\}$$

It is next supposed that the number of electrons or of positive ions produced is equal to $\beta \frac{dI(\nu)}{dz \cdot \sec \chi}$. Hence the number of electrons produced per second per unit volume is given by

$$q(\nu) = S \cdot A(\nu) \cdot I(\nu)_0 \rho_0 \text{Exp} \left\{ -\frac{z}{H} - A(\nu) \cdot \rho_0 \cdot H \cdot \sec \chi \cdot e^{-\frac{z}{H}} \right\}. \quad (3)$$

It is easy to see that $\beta = \frac{1}{h\nu}$, but Chapman does not attempt to define β and plots $q(\nu)$ as a function of z and thus gets a curve of variation of density of ions in the earth's atmosphere with height. His theory explains to some extent the variation of electron density of the ionized layers in the course of the day as observed in the radio experiments. Further he shows that the values of maximum electron density in winter and summer are related as

$$\frac{N_e^W}{N_e^S} = \left\{ \frac{\sin(\theta - \delta)}{\sin(\theta + \delta)} \right\}^{\frac{1}{2}}, \quad (4)$$

where δ is the declination of the sun and θ the colatitude of a place. This relation has been verified approximately by Appleton, Naismith and others (1935).

It should however be mentioned that it is not possible to arrive at an *absolute value* of $q(\nu)$ from Chapman's formula as the constant β is not precisely defined. Secondly, Chapman's theory holds only for *monochromatic radiation*, but if we suppose that the sun radiates like a black body, ionization will be produced by continuous radiation in the way supposed by Pannekoek. The values which Chapman obtains are not equilibrium values n_e of ionization density, but denote the *number of ions* produced per second by the radiation. But what we measure in radio experiments is the *equilibrium value*. For unicomponent systems, it can be shown (Appleton, 1938) that $n_e = (q/\alpha)^{\frac{1}{2}}$, but it is hardly correct to say that in the ionosphere we have to deal with a unicomponent system.

To show the connection between the two theories, let us first find out the relation between equilibrium value, the rate of production of ions and the rate of recombination. Let us take the simplified case of N_2 . As a result of reaction with sunlight, we can expect that the N_2 molecule will give rise to the following products:



Of these we can exclude the probability of the existence of N_2^- and N^- because, according to a large number of experiments with the mass-spectrograph, the existence of

such ions is doubtful (see for example Tüxen, 1936). We can also neglect N and N^+ since, on account of the high dissociation potential of nitrogen, it is rather improbable that there is an appreciable number of free nitrogen atoms and atom-ions present in the atmosphere. We are, therefore, left with only N_2 , N_2^+ and electrons. Even if some of these assumptions are proved to be incorrect, it does not interfere with the general line of argument followed in the present paper, as we propose here to deal with an idealized state only. Further, let us suppose that the ionization of N_2 proceeds in the same way as for the nitrogen atom, i.e. the ionization suddenly starts with a sharp maximum at the frequency corresponding to the ionization potential of N_2 and then falls off approximately as $1/\nu^3$ for higher frequencies, although it will be shown in another paper that these assumptions do not strictly hold for the ionization of the molecule.

Let us suppose that

$$N, n_+, n_e$$

are respectively the numbers per c.c. of neutral nitrogen molecules, ionized nitrogen molecules and electrons. We of course for the present assume that $n_+ = n_e$ (unicomponent system). We have then

$$\left. \begin{aligned} \frac{dN}{dt} &= -q + \alpha n_+ n_e = -q + \alpha n_e^2 \\ \frac{dn_e}{dt} &= q - \alpha n_+ n_e = q - \alpha n_e^2 \end{aligned} \right\}, \quad (5)$$

where q is the number of electrons or ions produced by sunlight per c.c. and α is the *recombination coefficient*.

When equilibrium has been established, we should have $n_e = (q/\alpha)^{1/2}$. In general, however, electrons arise not merely from the ionization of N_2 , but also from O_2 , O and probably N , hence the electron-concentration is to be regarded as an independent component. We shall not deal with this matter in this paper, but confine our attention only to calculation of the quantities q and α . We can easily obtain q from an extension of Chapman's method to continuous radiation. The number of ions produced by the absorption of radiation of intensity $I(\nu)$ is given by

$$q(\nu) d\nu = \frac{I(\nu) \cdot A(\nu) \cdot \rho \cdot d\nu}{h\nu} = \frac{N \cdot I(\nu) \cdot \tau(\nu) \cdot d\nu}{h\nu} = N I(\nu) \cdot \psi(\nu) \cdot d\nu, \quad (6)$$

because $I(\nu) \cdot d\nu \cdot A(\nu) \rho / h\nu$ is the number of quanta absorbed and each quantum produces one ion. To prove the relations stated here, we observe that

$A(\nu)$ = mass absorption coefficient = $\tau(\nu)/M$, where $\tau(\nu)$ is the absorption per atom, and M is the mass of the atom.

It will be seen that eq. (6) differs from eq. (3) in having β replaced by $\frac{1}{h\nu}$. Further we have as yet made no suggestion regarding the variation of N or $I(\nu)$ with height.

We have, therefore, for ionization by continuous radiation

$$q = \int_{\nu_0}^{\infty} q(\nu) \cdot d\nu = N \int_{\nu_0}^{\infty} I(\nu) \cdot \psi(\nu) \cdot d\nu. \quad (6')$$

According to Milne (1924), the recombination coefficient is given by

$$\alpha = \int_{\nu_0}^{\infty} 8\pi^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2} \frac{mv^2}{kT}} \{F(\nu) + I(\nu) \cdot G(\nu)\} \nu^3 \cdot d\nu.$$

By comparing the results obtained in the case of thermodynamical equilibrium and substituting $\frac{1}{2}mv^2 = h(\nu - \nu_0)$ this transforms into

$$\alpha = e^{\frac{h\nu_0}{kT}} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} \int_{\nu_0}^{\infty} \psi(\nu) \left\{ \frac{8\pi h\nu^3}{c^2} + I(\nu) \right\} e^{-\frac{h\nu}{kT}} \cdot d\nu. \quad (7)$$

Equating the value of $\alpha n_+ n_e$ with q , we have

$$K = K_0 \frac{\int_{\nu_0}^{\infty} \psi(\nu) \cdot I(\nu) \cdot d\nu}{\int_{\nu_0}^{\infty} \psi(\nu) \cdot e^{-\frac{h\nu}{kT}} \left\{ \frac{8\pi h\nu^3}{c^2} + I(\nu) \right\} d\nu}, \quad \dots \dots (8)$$

because $K_0 = \left(\frac{2\pi m kT}{h^2} \right)^{-\frac{3}{2}} e^{-\frac{h\nu_0}{kT}}$

is the value of the reaction-isochore, when radiation is at the same temperature with matter.

This is the original method of deduction by Milne of the equation of reaction-isochore under the conditions stated above. It is well known that assuming $\psi(\nu)$ to be given by C/ν^3 and taking $I(\nu)$ in the denominator to be negligible in comparison with $8\pi h\nu^3/c^2$, we arrive at Pannekoek's result, which will be discussed more in detail in section 5. We shall first of all calculate the rate of production of electrons, and the recombination coefficient according to formulae (6') and (8). For this purpose it is necessary to know how $\tau(\nu)$ varies with ν . This problem is discussed in the next section.

4. THE LAW OF PHOTO-ELECTRIC ABSORPTION

It is generally assumed (Pannekoek, 1926) that $\tau(\nu)$ varies according to the law first given by Kramers,

$$\tau(\nu) = \frac{16}{3} \frac{\pi^2 e^6}{\sqrt{3} c h^3} \mathcal{Z}^2 \frac{\nu_0}{\nu^3}. \quad (9)$$

Here ' $\mathcal{Z}$ ' is the effective charge on the nucleus, ν_0 is the threshold value of absorption frequency. If we wish to apply this formula to photo-ionization of atoms and to molecules like N_2 and O_2 , we have to introduce some assumption regarding the effective value of ' $\mathcal{Z}$ ', which is generally

understood to be the nuclear charge minus the 'screening constant' due to the effect of external electrons. Pannekoek (1926) and Chapman (1931) have introduced values for O and N -atoms, and N_2 and O_2 -molecules for which their papers may be consulted.

It is, however, doubtful whether Kramers' formula (9) which was first deduced on an older form of the quantum theory to account for X-ray absorption can at all be applicable to optical absorption. Rosseland (1936) comments 'One sometimes has the feeling that the applicability of the formula has been strained beyond the breaking point.'

The best course would be to take $\tau(\nu)$ values obtained from actual experiments. But as emphasized by Saha (1937), accurate experiments have not yet been performed for O_2 and N_2 ; and for O and N , probably the experiments would be extremely difficult. Under such circumstances, the best course appears to be to fall back upon wave-mechanical considerations.

For the H -atom, it has been shown by several authors [(for a comprehensive account, see Bethe (1932)], that (1) is given by

$$\tau(\nu) = \frac{2^8}{3} \cdot \frac{\pi e^2}{mc} \cdot \mathcal{Z}^3 \cdot \frac{\nu_0^3}{\nu^4} F\left(\sqrt{\frac{\nu_0}{\nu - \nu_0}}\right), \quad (10)$$

where $F(x) = \text{Exp}\{-4x \cdot \cot^{-1}x\} / (1 - e^{-2\pi x})$, and for moderate values of $\nu - \nu_0$, we have approximately (ν up to $3\nu_0$).

$$F(\nu) = \frac{\epsilon^{-4}}{3} \left\{ \frac{4\nu}{\nu_0} - 1 \right\}, \quad (10')$$

where ϵ is the base of natural logarithms.

We have from (10), and for $\mathcal{Z}=1$

τ_0 = limiting value of $\tau(\nu)$ at $\nu = \nu_0$

$$= \frac{2^8}{3} \cdot \frac{\pi e^2}{mc} \cdot \frac{1}{\nu_0} \epsilon^{-4} = \frac{2^7}{3} \frac{\epsilon^{-4} \cdot h^3}{\pi e^2 m^2 c} = 1.27 \times 10^{-17} \text{ cm}^2, \dots (11)$$

and $\tau(\nu) = \frac{\tau_0}{3} \left(\frac{4}{x^3} - \frac{1}{x^4} \right)$, where $x = \nu/\nu_0$. (12)

We have
$$\int_{\nu_0}^{\infty} \tau(\nu) d\nu = \frac{5}{9} \tau_0 \nu_0. \quad (13)$$

It will be interesting to compare the value of τ_0 obtained from (11) with that obtained from Kramers' formula. For the H -atom, we have $\mathcal{Z}=1$, and

$$\tau_0(\text{Kramers}) = \frac{4}{3\sqrt{3}} \frac{h^3}{\pi^2 e^2 m^2 c} = 3.98 \times 10^{-18} \text{ cm}^2, \quad (14)$$

$$\tau_0(\text{Wave-mechanics}) = \frac{2^5 \sqrt{3} \pi}{\epsilon^4} = 3.19 \tau_0(\text{Kramers}). \quad (15)$$

Kramers' value of τ_0 for the H -atom is therefore 3.19 times smaller than the wave mechanical value.

It should, however, be pointed out that the approximation (12) is only rough. This can be seen from a calculation of the oscillator strength for the continuous spectrum of hydrogen. According to a general theorem

$$f_c = \frac{g_i}{g_j} \cdot \frac{mc}{\pi e^2} \int_{\nu_0}^{\infty} \tau(\nu) \cdot d\nu = \frac{g_i}{g_j} \cdot \frac{\mathcal{Z}^2 \cdot 2^8}{3} \epsilon^{-4} \cdot \frac{5}{9} = .289 \cdot \mathcal{Z}^2. \quad (16)$$

Here

g_i = weight of the normal state of the H -atom; for H , it is 1s, $g_i=2$

g_j = weight of the final state of the H -atom; for H , it is ∞p , $g_j=6$.

The actual value of f_c for H is, however, .43. This discrepancy is due to our use of the approximation (12). The above formula for f_c holds only for the hydrogen-like atoms. But in the Upper Atmosphere, it is the following processes which give rise to electrons:



For calculating the ionization according to each of these processes, we require a knowledge of the corresponding $\tau(\nu)/\nu$ -curves. It can be assumed that for all atoms, the $\tau(\nu)$ curve is given by a formula of the type (10) or its approximate form (10') which we use here where $\mathcal{Z}$ is to be adjusted. In fact, Vinti (1933) has actually deduced theoretically such an expression for the continuous absorption by helium.

Molecular Ionization

But a little reflection shows that the same considerations cannot apply to molecules. For here ionization is attended usually with a change in the nuclear distance, e.g. in H_2 , the nuclear distance is $.75 \times 10^{-8}$ cm. while for H_2^+ , it is 1.071×10^{-8} cm. Hence according to the Franck-Condon principle, the value of $\tau(\nu)$ at the threshold potential is likely to be very small as the nuclear distances are very different. It will gradually rise to a maximum and then fall off. Probably the curve would be similar to that experimentally found by R. Ladenburg (1933) for the photo-dissociation of the O_2 -molecule by light of wavelength $< \lambda 1750\text{\AA}$; for Ladenburg's case, a theoretical expression has been found by Stueckelberg (1932). We shall not therefore, in this paper, discuss molecular photo-ionization at all.

Ionization of O and N -atoms

This leaves us only with the ionization of the O -atom and the N -atom. It has been surmised by several workers that the O_2 -molecule, in the course of the daytime, is completely broken up into atoms. Recently a theory of photo-dissociation of molecules has been worked out by Dr. R. C. Majumdar (1938) at the suggestion of the senior author, and making use of Ladenburg's figures for the

variation of the absorption-coefficient with ν , he has shown that O_2 in the daytime is completely broken up into atoms at a height of 150 kms.

The process $O+h\nu=O^++e$ therefore appears to be of great practical value in the production of electrons in the Upper Atmosphere in the daytime.

We shall now consider how Z^2 is to be obtained for the O and N -atoms.

We proceed from a general theorem by Thomas and Kuhn (see Bethe, *loc. cit.* p. 434):

$$\Sigma f_i + f_c = n, \quad (17)$$

where Σf_i is the sum of oscillator-strengths for line radiation, f_c is the oscillator strength for the continuous radiation at the end of the series limit, the initial state being the normal state of the atom, 'n' is the number of equivalent electrons which can perform the transition in question. In the case of the O -atom, the photo-ionization can be represented symbolically as

$$1s^2 2s^2 2p^4 \rightarrow 1s^2 2s^2 2p^3 \left\{ \begin{smallmatrix} \infty s \\ \infty d \end{smallmatrix} \right\}$$

to find out f_c , we have to find out Σf_i , for

$$2p^4 \rightarrow 2p^3 (ms, md)$$

transitions and over all values of m from $m=3$ to $m=\infty$.

This problem is difficult to solve, but it appears unlikely that Σf_i can be greater than unity. We can therefore put $f_c=3$ for the O -atom, and 2 for the N -atom approximately. This view is consistent with that of Herzfeld and Wolf (1925) who showed, from a discussion of the dispersion curves of Ne, A and other rare gases, that for a proper interpretation of the course of dispersion of these gases, we have to suppose that the characteristic frequency in the Lorentz-expression for dispersion is not given by the resonance line of the element, but by a line which lies in the region of continuous absorption by the atom and that the number of equivalent electrons per atom for inert gases is nearly 5. In other words, when we have a large number of equivalent electrons in any shell, the tendency for ionization proportionately rises. We assume that when an atom contains r equivalent electrons in the outermost shells, $f_c=r-1$ approx. provided r is large compared to unity. For helium, which contains two equivalent electrons, Vinti (1933) finds that $f_c=1.52$.

Z is now obtained from the formula for oscillator-strength

$$f_c = \frac{g_i}{g_j} \frac{mc}{\pi e^2} \int_{\nu_0}^{\infty} \tau(\nu) d\nu. \quad \dots \dots (18)$$

Substituting for $\tau(\nu)$ the value in (12),

$$f_c = \frac{g_i}{g_j} (\cdot 867) Z^2.$$

But there are further complications in the present cases. The normal oxygen atom has the electronic constitution $1s^2 2s^2 2p^4$ ($^3P_{210}$ 1D_2 1S_0), and the oxygen-ion has the constitution $1s^2 2s^2 2p^3$ ($^4S_{3/2}$ 2D 2P). The transitions contemplated, which cause ionization, can take place from any state of the normal O -atom to that of any normal O -ion provided this is permissible, and in the calculation of f_c , all such separate transitions must be taken into account.

The continuous transitions fall into the following groups:—

$$\begin{aligned} O^3P &\rightarrow O^+ (^4S)_{sd} \left\{ \begin{array}{l} f_{c_1} \dots I.P. \dots 13.55 \text{ volts.} \\ \rightarrow O^+ (^2D)_{sd} \left\{ \begin{array}{l} f_{c_2} \dots 15.86 \dots \\ \rightarrow O^+ (^2P)_{sd} \left\{ \begin{array}{l} f_{c_3} \dots 18.54 \dots \end{array} \right. \end{array} \right. \\ O^1D_2 \rightarrow O^+ (^2D)_{sd} \cdot f_{c_4} \dots \dots \dots \\ O^+ (^2P)_{sd} \dots f_{c_5} \dots \dots \dots \\ O^1S_0 \rightarrow O^+ (^2P)_{sd} \cdot f_{c_6} \dots \dots \dots \end{array} \right. \end{aligned}$$

The symbols (sd) denote that the hyperbolic orbit of the electron, which is released, may have $l=0$, or 2. This is necessary for calculation of the weight factors. We therefore expect (neglecting the small fine structure due to the presence of three 3P -states) that there will be six distinct continuous absorption curves corresponding to the six processes mentioned above. In fact, we have

$$f_c = 3 = f_{c_1} + f_{c_2} + \dots \dots \dots f_{c_6}.$$

To calculate the relative values of the quantities f_{c_i} , we can apply the arguments of Menzel and Goldberg (1936) about the parentages of the terms of the k -shell. According to these authors:—

$$\frac{f_{c_1} + f_{c_2} + f_{c_3}}{9 (=g \text{ of } ^3P)} = \frac{f_{c_4} + f_{c_5}}{5 (=g \text{ of } ^1D_2)} = \frac{f_{c_6}}{1 (=g \text{ of } ^1S_0)} = \frac{3}{15}$$

and

$$f_{c_1} : f_{c_2} : f_{c_3} = 4 : 10 : 6.$$

$$\text{Hence } f_{c_1} = \frac{9}{25}, f_{c_2} = \frac{9}{10}, f_{c_3} = \frac{27}{50}.$$

We have therefore from (16) for the process $O^3P \rightarrow O^+ ^4S$

$$Z^2 = \frac{g_j}{g_i} \frac{f_{c_1}}{\cdot 867} = \frac{48}{9} \frac{9}{25 \times \cdot 867} \dots \dots (19)$$

because

$$\begin{aligned} g_i &= \text{weight factor of } O^3P_{210} = 9 \\ g_j &= \text{weight factor of } (O^+ ^4S)_{sd} = 48 \end{aligned}$$

we get $Z=1.49$.

The value of τ_0 for the process $O^3P \rightarrow O^+ ^4S$ now becomes

$$\tau_0 = \frac{2^8}{3} \cdot \frac{\pi e^2}{mc} \cdot \frac{1}{\nu_0} \epsilon^{-4} \cdot Z^2 = 2.81 \times 10^{-17} \text{ cm}^2$$

The value given by Chapman is $2.5 \times 10^{-16} \text{ cm}^2$, i.e. nearly nine times larger.

We can, in a similar way, find out the effective values of Z for the processes

$$O^3P \rightarrow O^+ (^2D)_{sd}, \quad O^3P \rightarrow O^+ (^2P)_{sd}.$$

The g_j -value of $(O^+ {}^2D)_{sd}$ state is 120, and that for $(O^+ {}^2P)_{sd}$ is 72.

The corresponding Z -values are 3.04 and 2.36 respectively.

There will certainly be some difficulty in following why the effective nuclear charge in O should be different for the three processes mentioned above. But actually there is no difficulty as can be seen from the argument that $\tau(\nu)$ is given by the value of the transition-probability, from a certain initial (lower) state to a final state. Hence it will involve the effective nuclear charge for the initial as well as the final state. In fact, Z^2 should be replaced by $Z_i Z_f$. In these cases, though Z_i is identical, Z_f is different, as the electrons of the ion have different configurations, when giving rise to the different terms. Further, as it is a question of transition-probability, Z^2 may be widely different.

We have not calculated Z -values for transition from $O {}^1DS$ to $O^+ {}^2DP$ -states, as probably there are not sufficient $O {}^1DS$ -atoms in the ionosphere capable of producing any sensible ionization, for $O {}^1DS$ -atoms produced by any photo-electric process almost instantaneously revert to $O {}^3P$ -state.

The Nitrogen-atom

These considerations may now be extended also to the nitrogen-atom. We have now

$$f_c = 2.$$

The f_c -value is distributed as follows:—

$$\begin{aligned} N {}^2p^3 {}^4S \rightarrow N^+ {}^2p^2 ({}^3P)_{sd} \dots f_{c_1} \dots I.P. \dots 14.46 \text{ volts} \\ {}^2D \rightarrow N^+ ({}^2p^2 {}^3P)_{sd} \dots f_{c_2} \dots \\ N^+ ({}^2p^2 {}^1D_2)_{sd} \dots f_{c_3} \dots \\ {}^2P \rightarrow N^+ ({}^2p^2 {}^3P)_{sd} \dots f_{c_4} \dots \\ N^+ ({}^2p^2 {}^1D_2)_{sd} \dots f_{c_5} \dots \\ N^+ ({}^2p^2 {}^1S_0)_{sd} \dots f_{c_6} \dots \end{aligned}$$

We have

$$\frac{f_{c_1}}{4} = \frac{f_{c_2} + f_{c_3}}{10} = \frac{f_{c_4} + f_{c_5} + f_{c_6}}{6} = \frac{f_c}{20}$$

$$\text{and } f_{c_1} : f_{c_2} : f_{c_3} : f_{c_4} : f_{c_5} : f_{c_6} = 9 : 5 : 5 : 1 : 1 : 1.$$

Hence we have

$$f_{c_1} = 4, \quad Z = 3.53.$$

We need not calculate the Z -values for the other states of nitrogen, as practically all N -atoms will be in the 4S -state.

5. RATE OF PRODUCTION OF ELECTRONS BY PHOTO-IONIZATION

We shall now use the expression for $\tau(\nu)$ in formula (10) for the calculation of q according to the expression (6). We observe that if p be the partial pressure due to the absorbing particles at the region considered

$$I(\nu) = I(\nu)_0 \text{Exp} \left\{ -\frac{p\tau(\nu)}{Mg} \sec \chi \right\}, \quad (20)$$

when radiation is incident at an angle χ to the vertical, and $I(\nu)_0$ is the intensity of light just outside the earth's atmosphere. The relation (20) is proved as follows (first given by Pannekoek, 1926). On passing through a layer having the thickness dz (the layers are supposed to be parallel), the diminution in intensity is given by

$$dI(\nu) = -I(\nu) N\tau(\nu).dz.\sec \chi. \quad (21)$$

We have further the hydrostatic equation

$$dp = NgM dz, \text{ i.e., } NdZ = dp/gM. \quad (22)$$

Here M is the mass of each particle, and p is reckoned from the top of the atmosphere.

From (21) and (22) we have

$$\frac{dI(\nu)}{I(\nu)} = -\frac{\tau(\nu)}{gM} dp \sec \chi.$$

and on integrating this, we arrive at expression (20). It is easy to verify that for an isothermal layer, (20) reduces to (2), but (20) is more general. Substituting this in (6'),

$$q = N. \int_{\nu_0}^{\infty} I(\nu)_0 \cdot \psi(\nu) \cdot \text{Exp} \left\{ -\frac{p\tau(\nu)}{Mg} \sec \chi \right\} d\nu. \quad (23)$$

It is found rather difficult to integrate (23) rigorously on account of complexity of its form.

We can replace $\tau(\nu)$ within the integral (23) in the exponential by its mean value $\frac{1}{3}\tau_0$, where τ_0 is the value of $\tau(\nu)$ at the threshold frequency. We have then, taking the exponential term outside,

$$q = \frac{p}{kT} \text{Exp} \left\{ -\frac{5}{9} \cdot \frac{p\tau_0}{Mg} \sec \chi \right\} \cdot \int_{\nu_0}^{\infty} I(\nu)_0 \psi(\nu) \cdot d\nu.$$

Now as we have

$$I(\nu)_0 = \frac{8\pi\beta \cdot h\nu^3}{c^2} e^{-\frac{h\nu}{kT_s}}, \quad \psi(\nu) = \tau(\nu)/h\nu,$$

where $4\pi\beta$ is the solid angle subtended by the sun at the earth, $\beta = \frac{1}{230,000}$, T_s = temperature of the sun. The integral reduces to

$$\frac{8\pi\beta}{c^3} \int_{\nu_0}^{\infty} \nu^2 \cdot e^{-\frac{h\nu}{kT_s}} \tau(\nu) \cdot d\nu.$$

For $\tau(\nu)$, we can write the approximate value (12). Hence the integral

$$= \frac{8\pi\beta}{c^2} \cdot \frac{\tau_0 \nu_0^3}{3} \int_1^{\infty} \left(\frac{4}{x} - \frac{1}{x^2} \right) e^{-\mu_1 x} \cdot dx,$$

where $\mu_1 = \frac{h\nu_0}{kT_s}$. If we put $T_s = 6240^\circ\text{K}$ and ν_0 = ionization threshold frequency for the oxygen atom, it can be easily

seen that $\mu_1=25.78$ and for such large values of the index, it is easy to show that

$$\int_1^{\infty} \left(\frac{4}{x} - \frac{1}{x^2} \right) e^{-\mu_1 x} dx = \frac{3e^{-\mu_1}}{\mu_1}.$$

Hence we have

$$q = \frac{8\pi\beta}{c^2h} \cdot \tau_0 \cdot \nu_0^2 \cdot T_s \cdot e^{-\frac{h\nu_0}{kT_s}} \cdot \frac{p}{T} \cdot \text{Exp} \left\{ -\frac{5}{9} \frac{p\tau_0}{Mg} \sec \chi \right\}$$

$$= A \cdot \frac{p}{T} \cdot \text{Exp} \left\{ -\frac{p \cdot \sec \chi}{p_0} \right\}, \quad \dots \quad (24)$$

$$\left. \begin{aligned} A &= \frac{8\pi\beta}{c^2h} \cdot \tau_0 \cdot \nu_0^2 \cdot T_s \cdot e^{-\frac{h\nu_0}{kT_s}} \\ p_0 &= \frac{9}{5} \cdot \frac{Mg}{\tau_0} \end{aligned} \right\} \quad (25)$$

We can now try to find out the maximum value of q . Differentiating (24), we have

$$\frac{1}{q} \cdot \frac{dq}{dz} = \frac{dp}{dz} \left(\frac{1}{p} - \frac{\sec \chi}{p_0} \right) - \frac{1}{T} \frac{dT}{dz} \dots \dots$$

Let us first assume that $\frac{dT}{dz} = 0$, though we cannot be sure of the truth of this assumption. We have then

$$\frac{dq}{dz} = 0, \text{ when } p = \frac{9}{5} \frac{Mg}{\tau_0} \sec \chi = p_0 \cos \chi. \quad \dots \quad (26)$$

p_0 is the partial pressure at the place where we have maximum production of ions under vertical incidence. For incidence at an angle χ to the vertical, the maximum concentration is reached at the pressure $p = p_0 \cos \chi$.

Inserting this value of p in (24), we have for q_m , the maximum production of ions at angle χ , the expression

$$q_m = q_0 \cos \chi, \quad \dots \quad (27)$$

where q_0 = maximum production of the ions under vertical incidence, and it is given by

$$q_0 = \frac{A}{T} \cdot \frac{9}{5} \cdot \frac{Mg}{\epsilon \tau_0} = \frac{8\pi\beta}{c^2h} \cdot \frac{9}{5} \cdot \frac{Mg}{\epsilon} \cdot \frac{T_s}{T} \nu_0^2 e^{-\frac{h\nu_0}{kT_s}}. \quad (28)$$

We observe that q_0 is independent of τ_0 . This is because the smaller is the value of τ_0 , the higher is the partial pressure where maximum ionisation is reached.

The value of q , at a point where the pressure is p , is given by

$$q = q_0 y \text{ Exp} \{ 1 - y \sec \chi \}, \quad \dots \quad (29)$$

where $y = p/p_0$.

It can be easily shown that (29) yields us Chapman's expression for electron-production, if p is supposed to be given by the isothermal law

$$p = P \text{ Exp} \left\{ -\frac{h}{H} \right\},$$

where $H = \frac{kT}{Mg}$ = height of the homogeneous atmosphere, P = ground pressure.

For we can put, following Chapman,

$$p_0 = P \cdot \text{Exp} \{ -h_0/H \}, \quad z = (h - h_0)/H$$

so that $y = p/p_0 = e^{-z}$.

Then (29) becomes

$$q = q_0 \text{ Exp} \{ 1 - z - e^{-z} \cdot \sec \chi \}. \quad \dots \quad 30$$

This is the expression given by Chapman for variation of production of ions with height.

We have thus proved that even when photo-ionization is produced by continuous light, variation of ion-production with height continues to be given by Chapman's formula when T is supposed to be constant. Chapman proved the correctness of (30) for monochromatic light only. Further, and this is a definite advance on Chapman's result, we have now a perfectly definite expression for q_0 which is left undefined in Chapman's method of deduction.

We can now try to give some numerical calculations for q_0 and p_0 for the oxygen atom. As shown before, we have for the process

$$O \ ^3P \rightarrow O^+ \ ^4S, \quad Z = 1.49, \quad \nu_0 = 109837 \text{ c.}$$

Substituting these values in (25), we obtain

$$A = 3.71 \times 10^8, \quad p_0 = \frac{9}{5} \frac{Mg}{\tau_0} = 1.65 \times 10^{-3} \text{ dynes.}$$

$$q_0 = \frac{1.35 \times 10^5}{T}. \quad \dots \quad (31)$$

We have assumed that $T_s = 6240^\circ \text{K.}$

Appleton (1938) has calculated from the maximum electron-concentration curve that at Slough for an equinoctial day, when $\chi = 52^\circ$, $q_m = 78$, and for a midsummer day, i.e. for $\chi = 29^\circ$, $q_m = 88$. These values may be compared with those available from (31).

We have

$$q = q_0 \cos \chi = \frac{1.35 \times 10^5 \cos \chi}{T}$$

$$= 8.3 \times 10^4 / T \quad \dots \quad \text{for equinoctial noon}$$

$$= 11.8 \times 10^4 / T \quad \dots \quad \text{for midsummer noon.}$$

If we take T , the temperature for the F_2 -layer at noon 1065°K. , for an equinoctial day, and 1350°K. for a midsummer day, the above results are explained. These values are not inconsistent with the values now assigned to the temperature of the Upper Atmosphere (Appleton, 1935).

We have given these results with a certain amount of reserve; it must not be supposed that we commit ourselves to the opinion that the F_2 -layer is due solely to the ionization of O -atoms. We merely wish to point out that our calculations give us the right order of result.

Formula (7) gives us the recombination coefficient α . We can now neglect $I(\nu)$ in comparison to $8\pi h\nu^3/c^2$, and put for $\tau(\nu)$ the expression (12). We obtain after some work, for recombination between $O^+ {}^4S$ and e ,

$$\alpha = \frac{h}{(2\pi m)^{3/2} k^{1/2}} \cdot \frac{8\pi}{c^2} \cdot \tau_0 \nu_0^2 \cdot \frac{1}{T^{1/2}} \quad \dots \quad (32)$$

when we introduce the values of τ , ν_0 , for the process

$$O^+ {}^4S + e = O {}^3P, \quad \alpha = \frac{1.25 \times 10^{-10}}{T^{1/2}} = 6.3 \times 10^{-12},$$

provided $T=400^\circ\text{K}$. This value may be compared with the figures given by Appleton (1938), whose average values are nearly 10–20 times larger.

6. EQUILIBRIUM VALUE OF ELECTRON CONCENTRATION

The equilibrium value of electron concentration can now be easily calculated by putting for $\tau(\nu)$ the expression (12), in formula (8). We have now

$$K = K_0 \frac{\int_1^\infty \left(\frac{4}{x} - \frac{1}{x^2} \right) e^{-\mu_1 x} \text{Exp} \left\{ -\frac{p\tau_0}{3Mg} \left(\frac{4}{x^3} - \frac{1}{x^4} \right) \sec \chi \right\} dx}{\int_1^\infty \left(\frac{4}{x} - \frac{1}{x^2} \right) e^{-\mu_2 x} dx},$$

where $\mu_1 = \frac{h\nu_0}{kT_s}$, $\mu_2 = \frac{h\nu_0}{kT}$, $x = \nu/\nu_0$.

Now both μ_1 and μ_2 are large quantities. In fact, as we have seen, if we take $T_s = 6240^\circ\text{K}$, $\mu_1 = 26.9$, and for $T = 1000^\circ\text{K}$, $\mu_2 = 161.4$.

The quantity

$$\text{Exp} \left\{ -\frac{p\tau_0}{3Mg} \sec \chi \left(\frac{4}{x^3} - \frac{1}{x^4} \right) \right\}$$

within the upper integral can be replaced by its mean value

$$\text{Exp} \left(-\frac{5}{9} \frac{p\tau_0}{Mg} \sec \chi \right),$$

and taken outside as already described.

We can then easily show that

$$\begin{aligned} K &= K_0 \beta \cdot \frac{\mu_2}{\mu_1} e^{-(\mu_1 - \mu_2)} \text{Exp} \left\{ -\frac{5}{9} \frac{p\tau_0}{Mg} \sec \chi \right\} \\ &= \beta T_s T^{1/2} e^{-\frac{h\nu_0}{kT_s}} \left(\frac{2\pi mk}{h^2} \right)^{3/2} \text{Exp} \left\{ -\frac{5}{9} \frac{p\tau_0}{Mg} \sec \chi \right\}, \quad (33) \end{aligned}$$

which has the same form as the result deduced by Pannekoek. We have the factor $5/9$ instead of Pannekoek's $\frac{3}{4}$. From this expression, we can easily calculate the

maximum equilibrium value of electron concentration. We have according to (1)

$$K = \frac{n_+ n_e}{N} = \frac{q}{\alpha N},$$

and the last relation can be easily verified by reference to formulae (24) and (32) for q and α . If $n_+ = n_e$, as will happen in the case of unicomponent systems, we have $n_e = (q/\alpha)^{1/2}$. From this, it is clear, as α involves T only, and is independent of p , that in an isothermal atmosphere, the maximum value of n_e will occur at the same place as that for q . It is now easy to show that

$$\left. \begin{aligned} n_0 &= (q/\alpha)^{1/2} = \frac{2.55 \times 10^7}{T^{1/4}} \\ n_m &= n_0 (\cos \chi)^{1/2} \\ n_e &= n_m \gamma^{1/2} \text{Exp} \frac{1}{2} \{ 1 - \gamma \sec \chi \} \end{aligned} \right\} \quad \dots \quad (34)$$

where $\gamma = p/p_0$.

The variation of electron-density in the E and F_1 -layer is found to be given by the law $n = n_0 (\cos \chi)^{1/2}$ during hours of daylight. This is often cited (see Appleton, 1938) as proof of the correctness of Chapman's theory of simple region formation. But formulae (30) and (35) show that this relation holds good even when electrons are produced by continuous light.

7. IONIZATION BY MONOCHROMATIC LIGHT

In this section, we shall give a treatment of the ionization produced by monochromatic light, because it has been pointed out by several investigators that many upper air phenomena are probably due to ionization by monochromatic light from the sun. Maris and Hulburt (1929) talks of flares of ultraviolet radiation to account for magnetic storms, and abnormal display of aurora. One of us (Saha, 1935) has pointed out that the strong N_2^+ -ionization observed by Slipher (1933), in the morning and evening flash of sunlight in the Upper Atmosphere, is due to photo-ionization of N_2 due to emission lines of $He \text{ } 1s^2 {}^1S_0 - 1snp {}^1P$. Dellinger (1937) and others have tried to connect the sudden bursts of ionization which give rise to radio fade-outs in the sunlit part of the globe to the occurrence of disturbed regions on the sun showing strong H_α and H_β -lines in emission (vide further a note by R. N. Rai and K. B. Mathur, 1937).

The number of electrons produced by a monochromatic beam of intensity $I(\nu)$ is given by

$$q = N \cdot I(\nu) \cdot \psi(\nu) \cdot \Delta\nu.$$

Here $\Delta\nu$ is the equivalent breadth, N is the number of atoms or molecules in the region. Then we have

$$\text{since } I(\nu) = I(\nu)_0 \text{Exp} \left\{ -\frac{p\tau(\nu)}{Mg} \sec \chi \right\},$$

$$\text{and } N = p/kT$$

$$q = A' \frac{p}{T} \text{Exp} \left\{ -\frac{p \tau(\nu)}{Mg} \sec \chi \right\},$$

$$\text{where } A' = \frac{I(\nu)_0 \psi(\nu) \cdot \Delta \nu}{k}.$$

This expression is exactly similar to the expression (30) for ion-production by continuous light, but is considerably simpler. Here

$$A' = \frac{I(\nu)_0 \Delta \nu \tau(\nu)}{k \cdot h\nu}$$

is proportional to number of quanta absorbed per atom, and $\tau(\nu)$ has a perfectly definite value. The value of $I(\nu)_0$ depends upon the intensity of the light which may be available from astrophysical measurements, and the dimensions of the disturbed area on the sun. In case the disturbance extends over the whole surface, $I(\nu)_0$ is proportional to β but otherwise it will be much less, and will be equal to the solid angle subtended by the disturbed region in the earth's atmosphere.

We can find out q , q_m , q_0 as defined in sec. 5 exactly in the same way as there, and we have for an isothermal atmosphere

$$\left. \begin{aligned} q_m &= q_0 \cos \chi \\ q_0 &= \frac{A' gM}{T \epsilon \tau(\nu)} = \frac{I(\nu)_0 \Delta \nu gM}{h\nu \epsilon k T} \\ q &= q_0 y \text{Exp} \{1 - y \sec \chi\} \\ y &= p/p_0, \text{ where } p_0 = \frac{gM}{\epsilon \tau(\nu)} \end{aligned} \right\} \dots \dots (35)$$

Attention may be drawn to the expression for q_0 , the maximum electron-production per c.c. under vertical incidence—it is equal to the total number of ions produced by the total absorption of the beam divided by ϵH , where H is the height of the homogeneous atmosphere. This relation is identical with that obtained by Lenard and Chapman.

ABSTRACT

It has been shown that the two theories of upper air ionization, viz. that of Pannekoek and Chapman, are not essentially different from each other. When in the Chapman theory we give to the quantity β , which is introduced as a proportionality factor for deducing the number of electrons from the radiation absorbed, the value $\frac{1}{h\nu}$, and extend it to continuous radiation, we come to Pannekoek's results.

For absorption coefficient $\tau(\nu)$, a wave mechanical formula is used in the place of Kramers-expression. Rates of production of electrons from the O -atoms, the recombination co-efficient of ions and electrons, and equilibrium values of electron concentration are deduced for unicomponent systems. From these expressions, Chapman's formulae for variation of electron-production with height is deduced as a special case but the scope of the formula is found to be greater as it is found to hold not only for monochromatic light, as in Chapman's, but also for continuous light. Actual values of electron production at noon for the F -layer from the O -atom are given, and compared with figures given by Appleton.

It is further shown that the method is capable of giving also formula for electron production by monochromatic light, and yields results in terms of quantities which are physically definable.

REFERENCES

- Appleton, E. V. 1935a. *Nature*, **136**, 52.
 Appleton, E. V. and Naismith. 1935b. *Proc. Roy. Soc., A*, **150**, 685.
 Appleton, E. V. 1938. *Proc. Roy. Soc., A*, **162**, 451.
 Bethe. 1932. *Handbuch der Physik, Quanten*, 476.
 Chapman, S. 1931a. *Proc. Phys. Soc.*, **43**, 26, 1931b, *Proc. Roy. Soc.*, **132**, 353.
 Dellinger. 1937. *Terr. Mag.*, **42**, 49.
 Herzfeld and Wolf. 1925. *Ann. d. Physik*, (5), **76**, 71.
 Ladenburg and Van Voorhis. 1933. *Phys. Rev.*, **43**, 815.
 Lenard, 1911, *Sitzungsberichte d. Heidelberger Akad.*, **12**.
 Majumdar, R. C. 1938. *Ind. Journ. Physics*, **12**, 75.
 Maris and Hulburt. 1929. *Phys. Rev.*, **33**, 412.
 Menzel and Goldberg. 1936. *Astrophys. J.*, **84**, 1.
 Milne, E. A. 1924. *Phil. Mag.*, **47**, 209.
 Pannekoek, A. 1926. *Proc. Amsterdam Akad.*, **29**, 1165.
 Rai, R. N. and Mathur, K. B. 1937. *Science and Culture*, **3**, 338.
 Roosseland. 1936. *Theoretical Astrophysics*, 194.
 Saha, M. N. 1935. *Proc. Nat. Inst. Sci. Ind.*, **1**, 238.
 Saha, M. N. 1937. *Proc. Roy. Soc., A*, **160**, 155.
 Slipher. 1935. *M.N.R.A.S.*, **93**, 657.
 Stuckelberg. 1932. *Phys. Rev.*, **42**, 518.
 Tuxen, O. 1936. *Zeits. f. Phys.*, **103**, 463.
 Vinti, J. P. 1933. *Phys. Rev.*, **44**, 524.
 Woltjer. 1925. *Physica*, **5**, 406.

Note:—This paper was read before the Silver Jubilee session of the Indian Science Congress in January, 1938, but for unavoidable reasons it could not be sent for publication before April. While correcting the final proof it was brought to our notice by Dr. R. C. Majumdar that a paper had been published by E. O. Hulburt in *Phys. Rev.*, March, 1938, in which some of the results deduced in this paper have been obtained by a somewhat different procedure—(*M.N.S.* 15th July 1938).

71. THE PROPAGATION AND THE TOTAL REFLECTION OF ELECTROMAGNETIC WAVES IN THE IONOSPHERE

M. N. SAHA AND K. B. MATHUR

(*Ind. Jour. Phys.*, **13**, 251, 1939)

ABSTRACT

A critical review is given in this article of Prof. S. N. Bose's paper published in this journal. It is shown that when the collision frequency is taken to be zero, his method gives us the same result for the propagation of wireless waves as that of the earlier workers. The conditions of reflection which he has deduced for the case where collision cannot be neglected appear to require revision.

The propagation and the total reflection of electromagnetic waves in the ionosphere has been the subject of numerous investigations within the last ten years, a full bibliography of which is given under the references. A critical review of these papers shows that there are many points connected with this problem which have not yet received adequate explanation. In his pioneering work on the magnetionic theory, Appleton (1932) did not actually solve the relevant Maxwellian Equations but expressions were obtained for the refractive index from a calculation of the dielectric constant of the medium, which is supposed to consist of a number of free electrons and ions. The displacement of these under the magnetic field which is limited by collisions with neutral particles and positive ions constitutes the displacement current, which is necessary to calculate the complex dielectric constant. Appleton's method is usually known as the ray theory of propagation of the electromagnetic waves. The refractive index comes out in general to be a complex quantity and has two different values depending upon the state of polarisation of the wave. Further it is a function of the electron concentration and collisional frequency, both of which are functions of height. Consequently the wave equation becomes too complex for solution. From the analysis, it follows that the original wave splits up into two ordinary and extraordinary, which are propagated with different velocities, as in a doubly refracting medium. He supposes that in the case when collisions can be neglected, the wave gets reflected from the layer where the refractive index becomes equal to zero. This enabled him to obtain the conditions of reflection involving the electron concentration and the frequency of the wave, which are now well-known and have received verification at least in the case of the F-layer.

A number of other methods has been proposed of which we may mention that of Försterling and Lassen (1933), Saha, Rai and Mathur (1938) and that of Hartree (1931)

developed further by Booker (1935). The works of these authors lead to the same value of refractive index as that of Appleton, though originally they aimed at obtaining different results.

Recently Prof. S. N. Bose (1938) of Dacca has tackled the same problem by the method of characteristics, used for wave propagation by Hadamard, Debye and others. He confirms in general the conclusions of the previous investigators when collisions can be neglected, but gives new results when the collisions cannot be neglected. His results are, however, expressed in rather unfamiliar symbols, hence it is difficult to compare them with those of earlier workers and apply them to the elucidation of outstanding problems. The object of this paper is to examine his methods and results critically, to express them in a language easily comprehensible to workers on the ionosphere, and to find out how far the results obtained are new.

As we have to make a constant comparison between Bose's paper and the paper previously published by Saha, Rai and Mathur as well as those of other workers, we will refer to the latter as paper I.

The fundamental equations for propagation can be written as

$$\frac{1}{c} \frac{d\vec{E}}{dt} - \text{Curl } \vec{H} = -\frac{\rho \vec{V}}{c} \quad (1)$$

$$\frac{1}{c} \frac{d\vec{H}}{dt} + \text{Curl } \vec{E} = 0 \quad (2)$$

$$\text{Div } \vec{H} = 0 \quad (3)$$

$$\text{Div } \vec{E} = \rho \quad (4)$$

These equations may be compared with (1.1) of paper I.

Bose has used $\vec{E}$, while in paper I, $\vec{D}$ was used. But $\vec{D} = K\vec{E} + \vec{P}$, $K=1$, and $\vec{P} = N_e \vec{V}$, where $\vec{V}$ is the velocity of electrons. $\vec{P}$ is therefore the displacement current, a term denoted by Bose by the symbol θ . For his θ_0 , which is electrical density, we have used ρ . The fundamental equations used here, are

of the same form as those of Booker.⁵ The equations satisfy the conditions of continuity

$$\frac{d\rho}{dt} + \text{Div}(\rho \vec{V}) = 0. \quad (5)$$

Let us now suppose (see Bose, p. 122) that every quantity vary as e^S , where S is the phase. For a plane wave

$$S = ip \left[t - \frac{(lx + my + nz)}{c} \right]$$

where p is the pulsance $= 2\pi f$, f being the frequency of the wave, (l, m, n) direction-cosines of the wave-normal, q = refractive index. In general, (l, m, n) and q may be functions of (x, y, z) . Anyhow, no limitation is put on the form of S except that it is a function of (x, y, z, t) . Then the above equations reduce to

$$\frac{\dot{S}}{c} \vec{E} - (\vec{\Delta} S \times \vec{H}) = -\frac{\vec{P}}{c}. \quad (1')$$

$$\frac{\dot{S}}{c} \vec{H} + (\vec{\Delta} S \times \vec{E}) = 0. \quad (2')$$

$$(\vec{\Delta} S \cdot \vec{H}) = 0. \quad (3')$$

$$(\vec{\Delta} S \cdot \vec{E}) = \rho. \quad (4')$$

$$\dot{S}\rho + (\vec{P} \cdot \vec{\Delta} S) = 0. \quad (5')$$

Here the supposition is that if $\vec{E} = \vec{E}_0 e^S$, $\vec{E}_0$ is a slowly-varying function of (x, y, z, t) , i.e.,

$$E_0 \dot{S} \gg \frac{dE_0}{dt}, \quad E_0 S_x \gg \frac{dE_0}{dx}.$$

From (2), by scalar multiplication with $\vec{H}$, we have

$$(\vec{E} \cdot \vec{H}) = 0. \quad (6)$$

From (1), by scalar multiplication with $\vec{H}$, we have

$$(\vec{P} \cdot \vec{H}) = 0. \quad (7)$$

(4), (6), (7) show that $\vec{E}$, $\vec{P}$, $\vec{\Delta} S$ are all normal to $\vec{H}$, and hence lie in the plane perpendicular to $\vec{H}$. But neither $\vec{E}$, nor $\vec{P}$ are in general normal to $\vec{\Delta} S$, but from (1) we have

$$\frac{1}{c} (\vec{S}\vec{E} + \vec{P}) = (\vec{\Delta} S \times \vec{H}). \quad (8)$$

i.e., the vector $\vec{S}\vec{E} + \vec{P}$ is normal to both $\vec{\Delta} S$ and $\vec{H}$.

To find out $\vec{P}$, we take the equation of motion of the electrons and ions. Let the displacement of these particles

due to the radio-wave be $u = (\xi, \eta, \zeta)$. Then the equation of motion is

$$m\ddot{u} = eE - g\dot{u} + \frac{e}{c}(\dot{u} \times \vec{h}). \quad (9)$$

This is a vector equation, identical with equation (1.3) of our paper I, and equation on p. 131 of Bose. Now we have

$$\vec{P} = Ne\vec{u}, \quad \vec{P} = Ne\dot{u}.$$

Hence replacing $\vec{u}$ by $\vec{P}/Ne$, we have

$$\ddot{\vec{P}} + \nu \dot{\vec{P}} = \frac{Ne^2}{m} \vec{E} + (\dot{\vec{P}} \times \vec{h}). \quad (10)$$

Or using the symbols in (1.4) of paper I and putting $\vec{P} = \vec{P}_0 e^S$

$$\text{we have} \quad (\dot{S} + \nu) \dot{\vec{P}} = p_0^2 \vec{E} + (\dot{\vec{P}} \times \vec{p}_h). \quad (10')$$

where

$$p_h = \frac{eh}{mc}, \quad p_0^2 = \frac{Ne^2}{m}.$$

This is a vector equation and is equivalent to three different equations.

THE EQUATION OF PROPAGATION

Multiplying (20) by $\vec{\Delta} S$ vectorially, we have

$$\frac{\dot{S}}{c} (\vec{\Delta} S \times \vec{H}) + \vec{\Delta} S \times (\vec{\Delta} S \times \vec{E}) = 0.$$

since

$$(\vec{\Delta} S \times \vec{H}) = \frac{1}{c} (\dot{S} \vec{E} + \vec{P})$$

$$\begin{aligned} \vec{\Delta} S \times (\vec{\Delta} S \times \vec{E}) &= \vec{\Delta} S (\vec{\Delta} S \cdot \vec{E}) - E^2 (\vec{\Delta} S) \\ &= \rho \vec{\Delta} S - E^2 \vec{\Delta} S. \end{aligned}$$

Here $\vec{\Delta} S$ means $(\vec{\Delta} S)^2$. We have

$$\left(\frac{\dot{S}^2}{c^2} - \vec{\Delta} S \right) \vec{E} + \frac{\vec{P} \cdot \dot{S}}{c^2} + \rho \vec{\Delta} S = 0. \quad (11)$$

Now making use of the equations (5) and (10), we get the following vector-equation in $\vec{P}$

$$\frac{\vec{P} \cdot \dot{S}}{c^2} = \frac{1}{p_0^2} \left[\frac{\dot{S}^2}{c^2} - \vec{\Delta} S \right] \left[(\dot{S} + \nu) \vec{P} - (\dot{\vec{P}} \times \vec{p}_h) \right] = \frac{\vec{\Delta} S (\vec{P} \cdot \vec{\Delta} S)}{\dot{S}}. \quad (12)$$

This is equivalent to three equations, and the operations which we have carried out here is similar to those in § 2 of our paper I.

The three vector equations (12), can be written out in a form more convenient for work by introducing some

fresh notation. Here we are closely following Bose's procedure on pp. 137-138 of his paper.

We put

$$\left. \begin{aligned} g(S) &= \frac{\dot{S}^2}{c^2} - \Delta^2 S, \\ p(S) &= \dot{S}(\dot{S} + \nu) + p_0^2 \\ L(S) &= \left(\frac{\dot{S}^2}{c^2} - \Delta^2 S \right) \left[\dot{S}(\dot{S} + \nu) + P_0^2 \right] + P_0^2 \Delta^2 S \\ &= g(S) p(S) + p_0^2 \Delta^2 S. \end{aligned} \right\} \dots (13)$$

(12) can now be written as

$$L(S) \vec{P} - \dot{S} g(S) (\vec{P} \times \vec{P}_h) = p_0^2 \Delta S (\vec{P} \cdot \Delta S). \quad (14)$$

Writing out in full, we have

$$\begin{aligned} \dot{P}_x [L(S) - p_0^2 S^2] + \dot{P}_y [T_z - S_x S_y p_0^2] + \dot{P}_z [-T_y - S_x S_y p_0^2] &= 0 \\ \dot{P}_x [-T_z - S_x S_y p_0^2] + \dot{P}_y [L(S) - p_0^2 S^2] + \dot{P}_z [T_y - S_x S_y p_0^2] &= 0 \\ \dot{P}_x [T_y - S_x S_y p_0^2] + \dot{P}_y [-T_z - S_x S_y p_0^2] - \dot{P}_z [L(S) - S^2 p_0^2] &= 0 \end{aligned} \quad \dots (15)$$

where $\vec{T} = (T_x, T_y, T_z) = -\dot{S} g(S) \vec{p}_h$.

Since the equations hold simultaneously, the determinant of their co-efficients vanish. From this condition we get after some work

$$L^3(S) - L^2(S) \Delta^2 S p_0^2 + L(S) \dot{S}^2 g^2(S) p_0^2 - \dot{S}^2 g^2(S) p_0^2 (\Delta \vec{S} \cdot \vec{p}_h)^2 = 0 \quad \dots (16)$$

$$\text{Now} \quad (\Delta \vec{S} \cdot \vec{p}_h) = p_h \Delta S \cos \alpha,$$

where α is the angle between $\vec{p}_h$ the direction of the external magnetic field, and $\Delta \vec{S}$ the wave normal. Further, since

$$L(S) - p_0^2 \Delta^2 S = g(S) p(S),$$

we find that $g(S)$ cancels out as a common factor. Equation (16) reduces to

$$p(S) L^2(S) - \dot{S}^2 g(S) p_h^2 L(S) - \dot{S}^2 g(S) p_h^2 p_0^2 \Delta^2 S \cos^2 \alpha = 0 \quad \dots (17)$$

(16) and (17) are identical with the equations given by Bose on p. 142.

Bose points out that from equation (17), we can calculate the value of the refractive indices. As (17) is a quadratic equation we get two values for the refractive indices, q_1 and q_2 . But he does not proceed further to find out the actual values of q_1 and q_2 , and compare them with the results of earlier investigators. This we now proceed to do, and we shall show that we get the same value for q_1 and q_2 as obtained on p. 63 of paper I for the o- and x-waves.

Let us put

$$q = \frac{c |\Delta \vec{S}|}{\dot{S}} \quad \text{and} \quad \dot{S} = ip$$

This is equivalent to taking

$$S = ipt \mp \frac{ip}{c} \int q(ldx + mdy + ndz),$$

and for vertical propagation

$$S = ipt \mp \frac{ip}{c} \int q dz.$$

Now (ql, qm, qn) may be any functions of (x, y, z) ; q may be called the refractive index. $p = \frac{1}{i} \dot{S}$ is constant, and prescribed by the conditions of the experiment. Then it can be easily verified that if we put

$$1 - q^2 = x, \quad 1 - \frac{i\nu}{p} = \delta, \quad r = p_0^2/p^2,$$

we have for vertical propagation, i.e., $S_x = S_y = 0$, $S_z = 1$,

$$L(S) = -\frac{p^4}{c^2} (r - x\beta) \quad g(S) = -\frac{p^2}{c^2} x \quad p(S) = p^2 (r - \beta)$$

and equation (17) reduces to

$$C'x^2 + xr[2\beta(\beta - r) + \omega^2 \sin^2 \alpha] - r^2(r - \beta) = 0 \quad \dots (18)$$

Here C' is the quantity

$$C' = \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega^2 \cos^2 \alpha)$$

defined in equation (2.18) of paper I.

It can be shown after some work that the roots of equation (18) are given by

$$C'x = C'(1 - q^2) = -r\beta(r - \beta) - \frac{r\omega^2}{2} \sin^2 \alpha$$

$$\left[1 \pm \sqrt{1 + \frac{4(r - \beta)^2 \cos^2 \alpha}{\omega^2 \sin^4 \alpha}} \right]. \quad (19)$$

We get from (19)

$$C'q^2 = (r - \beta)(\omega^2 - \beta^2 + r\beta) - \frac{r\omega^2}{2} \sin^2 \alpha$$

$$\left[1 \pm \sqrt{\frac{4(r - \beta)^2 \cos^2 \alpha}{\omega^2 \sin^4 \alpha}} \right] \quad \dots (20)$$

If we neglect collisions, i.e., put $\beta = 1$, we can easily deduce that (20) reduces to the values of q_o and q_x given in (3.10) of paper I. Hence we have proved that for vertical propagation, Bose's treatment gives the same result as that of earlier workers.

CONDITIONS FOR REFLECTION OF THE E. M. WAVE FROM THE IONOSPHERE

Let us now critically examine Bose's work as far as it deals with the conditions of reflection of the o- and x-waves from the ionosphere. In the original treatment of Appleton, it was supposed that the waves get reflected when q , the refractive index, becomes zero, in the cases where collision

frequency can be neglected. This gives the well-known conditions of reflection.

$$\text{o-wave} \quad \frac{Ne^2}{m} = p^2; \quad \dots (21)$$

$$\text{x-wave} \quad \frac{Ne^2}{m} = p^2 \pm pp_h.$$

It is supposed that the reflection represented by + sign does not occur, as the x-wave gets totally reflected from a lower height corresponding to the negative sign. Under these suppositions, we should have for Allahabad for $f=4$ Mc/sec.

$$f_c^o - f_c^x = 65 \text{ Mc/sec.}$$

While this has been verified in general, Pant and Bajpai (1937), at Allahabad obtained on several occasions, difference of a quite different order:—it was found that for $f=4$ Mc/sec.

$$f_c^o - f_c^x = 14 \text{ Mc/sec.}$$

This was explained by R. N. Rai (1937) from the idea that waves are returned from the ionosphere, when their group-velocity of propagation becomes zero. From this, he deduced when collisions can be neglected, in addition to the Appleton conditions, a new condition of reflection

$$\frac{Ne^2}{m} = p^2 \frac{p^2 - p_h^2}{p^2 - p_L^2}. \quad \dots (22)$$

This gives us exactly

$$f_c^o - f_c^x = 14 \text{ Mc/sec.}$$

Thus the new condition explains completely the result obtained by Pant and Bajpai.

The question now rises: Both Appleton's criterion ($q=0$), as well as that used by Rai (group-velocity=0) are, at best, assumptions. Can they be substantiated as direct deductions from theory? Further, when the collisional damping cannot be neglected, what will be the condition of reflection? This is the problem which Bose sets about to solve. His procedure is as follows:

By squaring equation (2), we have

$$\frac{\dot{S}^2}{c^2} H^2 = (\Delta S \times E)^2 = (\Delta S)^2 E^2 - (\Delta S \cdot E)^2.$$

$$\text{Hence} \quad \frac{H^2}{E^2} = \frac{c^2 \Delta^2 S}{\dot{S}^2} - \frac{(\Delta S \cdot E)^2 \cdot c^2}{E^2 \cdot \dot{S}^2} = q^2 (1 - \cos^2 \theta), \quad \dots (23)$$

where θ is the angle between ΔS and E . In general, θ is a definite quantity.

Bose has assumed that reflection takes place when $H=0$ or when E becomes parallel to ΔS . These conditions reduce to $q=0$ and $q=\infty$ respectively.

From (23) we have

$$\begin{aligned} H=0, & \quad \text{when } q=0, \\ \text{and } E=0, & \quad \text{when } q=\infty. \end{aligned}$$

The propagation loses its wave character either when $H=0$, or $E=0$. We can therefore suppose that the wave will be reflected either when $q=0$, or $q=\infty$. The former gives us the conditions of Appleton (equation 21), and the latter gives us Rai's condition.

Bose has further tried to obtain more general conditions of reflection when damping cannot be neglected. (Equations on p. 132, 133 again on p. 139 and 140.). His condition for the o-wave is

$$\frac{dS}{dt} = -\frac{\nu}{2} \pm i\sqrt{p_0^2 - \nu^2/4}. \quad \dots (24)$$

He concludes that from this the train totally reflected has the form

$$\text{Exp} \left[-\frac{\nu}{2} t \pm i\sqrt{p_0^2 - \nu^2/4} t \right],$$

and puts

$$p_c^2 = p_0^2 - \nu^2/4.$$

This takes the place of $p^2 = p_0^2$ for the o-wave.

Similarly he obtains results for the x-wave on p. 133, and 135, which take the place of

$$p_0^2 = p^2 \pm pp_h, \quad p_0^2 = p^2 \frac{p^2 - p_h^2}{p^2 - p_L^2}.$$

These results obtained by Bose are equivalent to putting the complex values of q for the o and x-waves given by formula (20) equal to zero and infinity. This is shown in Appendix (1), and the work is due to Mr. R. N. Rai.

But it is difficult to agree with this procedure because when q is complex, the conditions of reflection are no longer given by either $q=0$, or $q=\infty$.

For in general, when q is complex we can put $q = \mu + i\frac{ck}{p}$.

and it has been shown, that we have for the quasi-transverse as well as quasilongitudinal regions

$$\mu^2 = \frac{1}{2} \left\{ \sqrt{X^2 - Y^2} + X \right\}, \quad \dots (25)$$

$$\frac{c^2 k^2}{p^2} = \frac{1}{2} \left\{ \sqrt{X^2 + Y^2} - X \right\},$$

where X and Y are functions of electron-concentration, and collisional damping. For the o-wave in the equatorial region, we have

$$X = 1 - \frac{r}{1 + \delta^2}, \quad Y = \frac{r\delta}{1 + \delta^2}.$$

The forms (25) show that μ^2 and $\frac{c^2 k^2}{p^2}$ can never be

negative. This is at once clear if one looks at the curves drawn for various values of ν , and r by M. Taylor (1938) and Goubau (1935). For the o-wave it is found that for a fixed value of ν , μ gradually decreases with r , and ultimately takes a small value > 0 , and varying very slowly. For the x-wave, the first part of the curve is similar, but

then μ rises abruptly, reaches a steep maximum at the point corresponding to $\mu=\infty$ and then drops out very much as in the μ -curve for the o-wave.

But it should be emphasised that these curves give no idea of the actual variation of μ^2 with z , because μ^2 is a function of N (the number of electrons), and ν , the collision damping, both of which vary continuously with height. For finding out the actual variation of μ^2 with height, we can adopt two procedures—we can take a number of curves of the type drawn by Goubau or M. Taylor for varying values of ν , plot them on cardboards, and then cut the cardboards along the curves. These may then be arranged in a three-dimensional array, behind each other, so that X-axis corresponds to N , the Y-axis to ν , and the Z-axis to μ^2 . We have then to take a section through the three dimensional profile of the μ^2 -surface, corresponding to the actual conditions in the atmosphere.

The other procedure would be to plot μ^2 -values taking some theoretical values for ν and N , the electron concentration. N can be calculated from Chapman's formula for a simple region which has been shown by Saha and Rai (1938) to hold for the general case when radiation need not be monochromatic and ν can be calculated from the kinetic gas theory, by taking $T=\text{constant}$, or T varying according to some assumed law.

In general, $\mu^2=1$ in the non-deviating region, and variations will occur only in the deviating region. The curve will be usually smooth, but may show sudden fluctuations when we pass through irregular banks of ions or electrons, such as may likely be produced by minor causes. When we come to the simple region, μ^2 will vary continuously from unity to a small value, depending on p . These calculations are being carried out by the junior author.

These arguments tell us that both μ^2 and $\left(\frac{c^2 k^2}{p^2}\right)$ the real and imaginary parts of q , are essentially positive, and they can be zero, only in the ideal case when δ , the collision frequency is zero. Hence it is not possible to put $q=0$, and deduce any condition from it. In the same way, we cannot put $q=\infty$, when q is complex.

REFERENCES

- Appleton (1932): *J. Elec. Engrs.*, **71**, 642.
 Booker (1936): *Proc. Roy. Soc. A.*, **155**, 235.
 Bose (1938): *Ind. Journ. Phys.*, **21**, 121.
 Försterling & Lassen (1933): *Ann. d. Physik.*, **18**, 26.
 Goubau (1935): *Zs. f. H. F. T.*, **45**, 181.

- Hartree (1931): *Proc. Camb. Phil. Soc.*, **27**, 143.
 Pant & Bajpai (1937): *Science & Culture*, **2**, 409.
 Rai (1937): *Proc. Nat. Inst. Sci. India*, **3**, 307.
 Saha, Rai & Mathur (1938): *Proc. Nat. Inst. Sci. India*, **4**, 53.
 Taylor (1933): *Proc. Roy. Soc.*, **45**, 245.

APPENDIX - I

Equation (20) can be written as

$$C' q_0^2 = t(w^2 + \beta t) - \frac{rw^2}{2} \sin^2 \alpha \left[1 - \sqrt{1 + \frac{4t^2 \cos^2 \alpha}{w^2 \sin^4 \alpha}} \right], \dots (i)$$

$$C' q_x^2 = t(w^2 + \beta t) - \frac{rw^2}{2} \sin^2 \alpha \left[1 + \sqrt{1 + \frac{4t^2 \cos^2 \alpha}{w^2 \sin^4 \alpha}} \right], \dots (ii)$$

where $t=(r-\beta)$. Now $q_0^2=0$, when $t=0$, or $r-\beta=0$, or $p^2 - ivp - p_0^2 = 0$, or $p = \frac{iv}{2} \pm \sqrt{p_0^2 - \nu^2/4}$.

Therefore the critical frequency is given by

$$p_c = \sqrt{p_0^2 - \nu^2/4}. \dots (iii)$$

$q_x^2=0$ when $t^2=w^2$, or $t=\pm w$, or $p^2 - ivp - p_0^2 \pm pp_h = 0$.

Putting $p' = p - \frac{iv}{2} \pm \frac{p_h}{2}$, we have $p'^2 = \frac{p_h^2}{4} - \frac{\nu^2}{4} \mp \frac{ivp_h}{2} + p_0^2 = (a+ib)^2$,

where

$$a = \left[\frac{1}{2} \left\{ \frac{p_h^2}{4} - \frac{\nu^2}{4} + p_0^2 + \sqrt{\left(\frac{p_h^2}{4} - \frac{\nu^2}{4} + p_0^2 \right)^2 + \frac{\nu^2 p_h^2}{4}} \right\} \right]^{\frac{1}{2}}. (iv)$$

The critical frequency is given by

$$p_c = a \mp p_h/2. \dots (v)$$

q_0^2 and q_x^2 are equal to infinity when $C'=0$

$$\text{or} \quad \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega^2 \cos^2 \alpha) = 0.$$

After simplification and rearrangement, we have

$$ip(ip + \nu) + \frac{p_0^2[(ip + \nu)^2 + p_h^2 \cos^2 \alpha]}{[(ip + \nu)^2 + p_h^2]} = 0,$$

which reduces to

$$p_0^2 = p^2 \frac{p^2 - p_h^2}{p^2 - p_h^2 \cos^2 \alpha}, \dots (vi)$$

when $\nu=0$.

Here we see that the conditions (iv), (v), (vi) are the same as those obtained by Bose.

72. ON THE STRUCTURE OF ATOMIC NUCLEI

M. N. SAHA, S. C. SIKKAR AND K. C. MUKHERJEE

(*Proc. Nat. Inst. Sci. Ind.*, **6**, 45, 1940)

(Received January 16, 1940)

Ever since Heisenberg (1932) showed that the nucleus of the atom is to be regarded as composed of two fundamental particles, viz., the proton and the neutron, many investigations from the theoretical point of view have been carried out regarding the structure, stability and reactivity of nuclei. In the meantime, there have been large additions to the known number of nuclei by (1) the discovery of newer and rarer stable isotopes, and (2) the discovery of new unstable varieties of isotopes produced by bombardment of known nuclei by means of α -particles, deuterons, protons, neutrons and to a slight extent by photons. The recent discovery of fission of uranium and thorium by neutrons has led to the discovery of a number of β^- -active nuclei which probably could not have been produced by any other existing method.

The enormous increase in our knowledge of nuclear phenomena within the last eight years has rendered it almost impossible for the average physicist to form a comprehensive picture of the present situation, much less than keep in living touch with progressing knowledge.

In this paper, an attempt has been made to present the existing knowledge of the known nuclei, stable, as well as radioactive, in the form of a chart. No attempt has been made to give any theoretical discussion on stability in this paper, but rules and regularities which are obvious have been duly noted and recorded. Probably we are justified, at this stage, in adopting this attitude in view of the following significant remark we came across in Gamow's 'Structure of Atomic Nuclei' (1938).

'One may hope that further investigations along these lines will add considerably to our understanding of more detailed problems of structure. Much has already been done with rather overlapping results by Bartlett, Gapon, Ivanenko, Elsasser, Guggenheimer and others; it is not referred to in detail here because the author was never able in studying these articles to remember the beginning when he was reading the end.'

Symbols used

We denote by

p .. the proton,
n .. the neutron,

Z .. the nuclear charge,
N .. the number of neutrons,
A .. the mass-number, so that
 $A = Z + N$.

$I = N - Z = A - 2Z$ has been called the 'Isotope-number' by Bethe and Bacher (1936).

According to this notation

$p^Z n^N$ or $p^Z n^N$ denotes a nucleus composed of Z protons and N neutrons. Thus ${}_{38}\text{Sr}^{87}$ is $p^{38}n^{49}$, i.e. strontium 87 would be found in the isotope line $I=11$ of our chart.

In this connection, a comparison may be made between the chart given here and the other charts so far in use. Papers earlier than 1931 were written on the supposition that the nucleus was composed of protons and electrons. Nevertheless, many of the conclusions and regularities noted in earlier papers are very valuable, and have been utilized by subsequent workers:

(1) W. D. Harkins (1928) plotted an (I/Z) -curve in fig. 14, p. 113, and nuclei were classified into a few groups.

(2) Barton (1930) plots an (N/Z) -diagram up to $Z=61$, and notes a few regularities.

(3) W. D. Harkins (1931) plots an (N/Z) -diagram (fig. 1) and a number of (I/Z) -diagrams (figs. 2, 3, 4, 5) and an $(N/P)/Z$ -diagram.

(4) Heisenberg (1932) first took the view that the nucleus is composed of neutrons and protons. He discussed nuclear stability by plotting $(N/Z)/Z$ -diagrams.

(5) Gamow (1934) utilized $(N/Z)/Z$ -diagrams for a discussion on nuclear stability and α - and β -emissions.

(6) Guggenheimer (1934) plotted an (N/Z) -diagram and classified nuclei into groups.

(7) Bethe and Bacher (1936) give on p. 97 an I/A -diagram on a small scale, comprising only stable nuclei. No isotopic lines (Z -lines) have been drawn, but some regularities regarding the stability of nuclei have been pointed out.

None of the above workers included β^{+-} -emitting nuclei in their diagrams.

(8) Hevesy and Levi (1936-37) have given a number of (I/Z)-diagrams of stable and radioactive isotopes.

(9) H. Brown (1938) has plotted an (I/Z)-diagram for finding out the range of occurrence of stable isotopes.

(10) Gregoire (1938a) has an (A/Z)-diagram for presenting the totality of our knowledge of nuclei, stable as well as radioactive. (The same diagram has been drawn more elaborately in '*Physique Nucleaire*' of *Tables Annuelles de Constant et Donnée's Numeriques* No. 26, 1938). Here the radioactive nuclei have been drawn in different colours, and percentages of isotopes have been indicated.

(11) In their paper on 'Mechanism of Nuclear Fission', Bohr and Wheeler (1939) published an (I/A)-diagram (Fig. 8, p. 445) for illustrating 'Nuclear Fission'. This paper came to our notice after our work was almost over. This figure contains only stable nuclei and is identical in principle with ours, but it has been drawn for a limited range, and for illustrating the successive β^- -emission products of fission of the uranium nucleus.

Explanation of the chart

The abscissa represents mass-number A, the ordinate represents I, the isotope number. The parallel lines at 45° , to be henceforward called the Z-lines, represent atomic number 'Z'. Thus all isotopes of element 'Z' are to be found on the same 'Z'-line. Each isotope is represented by a circle. Solid circles represent 'Stable' nuclei. Hollow circles with an arrow pointing up, δ , represent β^+ -emitting (positron) nuclei; when the arrow points down, φ , they indicate β^- -emitting (electron) nuclei. Circles with arrows pointing both up and down, ξ , like ${}_{90}\text{Cu}^{64}$ indicate that the nuclei are both β^+ and β^- -active. The percentage occurrence of any nucleus is given by the number on the top. For isotopes having small abundance, the actual percentage is given to the nearest fraction. The half lives of β -particle-emitting products are indicated. The following abbreviations have been used for indicating the half lives:

s	..	..	seconds,
m	..	..	minutes,
h	..	..	hours,
d	..	..	days,
mo	..	..	months,
y	..	..	years.

The nuclei represented by φ denote those obtained by fission of U or Th.

The reader may now refer to the symbolic diagram on the left of Chart 1. The N.W.-pointing arrow terminating in p denotes a proton-emission; an arrow in the opposite direction (S.E., not shown in fig.) denotes a proton-capture.

Similarly, the S.W.-pointing arrow ending in n denotes neutron-emission, and an arrow in the opposite direction (N.E., not shown in fig.) would denote a neutron-capture.

The west-pointing double-arrow terminating in α denotes an α -particle-emission.

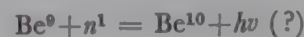
Thus we can follow the reaction



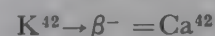
in the chart by putting our finger on B^{10} , and going diagonally downwards (S.E.) we reach C^{11} , and we find that C^{11} will emit a positron, and going vertically upwards we reach the stable nucleus B^{11} .

'Neutron-capture' takes a nucleus a step higher along the Z-line.

Thus



We can follow this reaction easily in the chart. Let us take a reaction in which a nuclear particle is emitted, e.g.,



We put our finger on Ca^{42} —a neutron bombardment of Ca^{42} followed by capture takes us to C^{43*} along the Z-line,* denoting that it is an intermediate nucleus, of extremely short life, breaking up into K^{42} and H^1 . K^{42} is obtained by going diagonally up in the p -direction. The chart shows that K^{42} is β^- -active and changes to Ca^{42} .

Deuteron-bombardment

Deuteron bombardment followed by capture will take a nucleus along the I-line (horizontal or East) to the next nucleus, and the chart tells us what reactions are to be expected. Thus

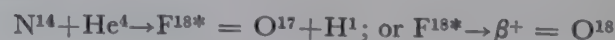


We put our finger on Si^{30} ; capture of H^2 takes us to P^{32*} intermediate, which breaks up into Si^{31} and H^1 . The chart shows that Si^{31} emits a β^- -particle and gives us P^{31} . Thus starting from Si^{31} one goes vertically one step downwards and reaches P^{31} . The reaction $\text{P}^{32} \rightarrow \beta^- = \text{S}^{32}$ is also possible, but its probability seems to be negligibly small.

α -ray bombardment

α -ray bombardment followed by capture will take a nucleus along the I-line two steps to the right; and *vice-versa*, if in a reaction, an α -ray is emitted, the nucleus will have to be taken two steps to the left along the same I-line.

Thus



Thus we see that N^{14} on capturing He^4 will form an intermediate nucleus F^{18*} , which can either break up into O^{17} and H^1 , or emit a β^+ -particle, and pass on to O^{18} . The former process is, however, much more probable and is observed usually.

For illustrating the use of the chart, we take sulphur,

CHART 3



$Z=16$. A glance at the Z-line 16 shows that sulphur has the following isotopes:

S^{31}	S^{32}	S^{33}	S^{34}	S^{35}	S^{36}	S^{37}
+	95	·7	4	—	·02	—
26m (?)				88d		5m

S^{31} is β^+ -active, with half life of 26m. ? indicates that the estimate is doubtful. S^{35} , S^{37} are β^- -active, with half lives 88 days and 5 min. respectively. S^{32} , S^{33} , S^{34} , S^{36} are stable isotopes occurring in the proportion 95 : ·7 : 4 : ·02.

The symbol δ indicates that the nucleus $p^z n^{z+1}$ does not actually emit a positron, but captures a K-electron, and passes on vertically up to the nucleus $p^{z-1} n^{z-1+1+2}$.

A glance at the chart at once shows its usefulness. It not only comprises all our present knowledge about isotopes, stable as well as radioactive, but, as will be shown presently, indicates definite rules for stability and for electron- and positron-emission. Further, it suggests new nuclear processes and predicts new stable isotopes, not yet discovered. For purposes of clarity, a number of I-lines at intervals of '5' have been drawn. These have no special significance.

Rules for Stability

For discussing this point, we have taken each horizontal row, corresponding to definite values of 'I'.

If we take $I=0$, we find that the nuclei are stable from $Z=1$, H^2 , to $Z=8$, O^{16} . After that, the nucleus is stable for even values of Z , and β^+ -active for odd values of Z . The group stops with Sc^{42} , which is β^+ -active.

(Rule 1).

When I is even and > 2 , we get alternation of stable and β -active nuclei. Stable nuclei are obtained for *even* values of Z , and β -active nuclei are obtained for *odd* values of Z . This rule is partly foreshadowed in a remark by Bethe and Bacher (1936, p. 104) and has been discussed in detail in §10, p. 100.

Illustration

Let us take $I=4$. We get the following:—

$I=4; Z=$	16	17	18	19	20	21	22	23
	S^{36}	Cl^{38}	A^{40}	K^{42}	Ca^{44}	Sc^{46}	Ti^{48}	V^{50}
	stable	—	stable	—	stable	—	stable	+
$Z=$	24	25	26	27	28	29	30	31
	Cr^{52}	Mn^{54}	Fe^{56}	Co^{58}	Ni^{60}	Cu^{62}	Ni^{64}	Ga^{66}
	stable	+-	stable	+	stable	+	stable	+

We observe that after approximately the middle of the series is passed, the nuclei to the right with odd Z become β^+ -active. This rule is found to be obeyed right up to $I=40$, after which we enter the region of natural radioactivity, where also up to $I=54$, the rule is generally obeyed with a few exceptions (noted later).

For $I=2$, we observe that the first stable nucleus is $Z=8$, O^{18} , after which the rule of alternation holds all right. Before $Z=8$, we have a number of β^- -emitting nuclei from $Z=1$ to $Z=7$. It is quite possible that in the other groups also, *e.g.* for the group $I=4$, we may have a number of β^- -active elements before S^{36} , but special reactions will have to be devised to obtain them.

(Rule 2). I is odd:

In these groups, we first find β^- -active nuclei, and then arrive at a number of succeeding stable nuclei. These are followed by β^+ -active nuclei. The number of succeeding stable nuclei has been found sometimes as small as 3, sometimes as large as 13, usually the nucleus in the midst of the stable group appears to be the most stable, though there appear to be exceptions.

Illustration

Let us take $I=5$. A glance at the chart shows that we have

$I=5; Z=$	16	17	18	19	20	21	22	23
	S^{37}	—	A^{41}	K^{43}	Ca^{45}	—	Ti^{49}	V^{51}
	—	—	—	—	—	—	6,	100,
$Z=$	24	25	26	27	28	29	30	31
	Cr^{53}	Mn^{55}	Fe^{57}	Co^{59}	Ni^{61}	Cu^{63}	Zn^{65}	Ga^{67}
	10,	100,	2,	99·8	1,	68,	+	+
$Z=$	32	33						
	Ge^{69}	As^{71}						
	+	+						

The stable nuclei start from Ti^{49} and extend up to Cu^{63} . The numbers below them here show the percentages. The elements to the left of the stable group are β^- -active and those to the right are β^+ -active. We have some gaps, *e.g.*, at Cl^{39} (β^-), Sc^{47} (β^- or stable), but these will probably be discovered if proper nuclear reactions are tried.

We now begin a detailed discussion of the table, taking each I-line in turn. While studying these discussions, the reader is advised to have the chart at hand, as all references are to the chart.

$I=-2$:

A few nuclei like Li^4 have been postulated, but as knowledge about them is very meagre, we leave this group for the present out of our consideration.

$I=-1$:

In this line, H^1 , He^3 (Alvarez and Cornog, 1939) are stable. Li^5 cannot be formed, energy-considerations are against it.

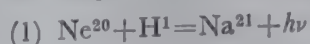
Absentees are:— Na^{21} , P^{29} , Cl^{33} , A^{35} , K^{37} which are expected to be β^+ -active.

The series terminates at Sc^{41} .

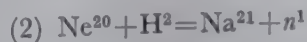
It is probable that the 'absentee' nuclei may be obtained

if proper nuclear reactions are tried. Let us take an example.

For Na^{21} , the following reactions are suggested:—



This is suggested in analogy to the reaction $\text{O}^{16} + \text{H}^1 = \text{F}^{17} + h\nu$ which has been observed by DuBridge *et al* (1937, 1938).



This is suggested in analogy to the reaction $\text{O}^{16} + \text{H}^2 = \text{F}^{17} + n^1$, observed by Kurie *et al* (1936) and Newson (1937). But the reaction has been tried by Snell (1937) who, however, obtained $\text{Ne}^{20} + \text{H}^2 = \text{F}^{18} + \text{He}^4$. Probably the chance of capture followed by γ -emission is negligible to that of particle emission, as has been found by Bethe (1939).

It is clear from this discussion that the suggestion of proper reaction to get a certain absentee nuclei will involve a good deal of work. Hence the subject is not further pursued in this paper.

It is not yet clear whether there will be any limit to the number of nuclei on any I-level. The last nuclei for $I = -1$ is Sc^{41} . It is possible that we may get the series continued to Ti^{43} , V^{45} , etc . . . , but the prospect of getting such nuclei will be diminished with larger Z , as no stable nuclei, which can act as the starting material for bombardment with H^1 , He^4 and n^1 will be available.

$I=0$:

This line starts with H^2 and is stable up to O^{16} , after which the alternation rule holds: Nuclei are stable for $Z=\text{even}$, and β -active for $Z=\text{odd}$. The series terminates for Sc^{42} , but we have, after a long interval, Cu^{58} , which is stated by Delsasso (1939) to be β^+ -active. The intermediate absent nuclei are:—

Ti^{44}	V^{46}	Cr^{48}	Mn^{50}	Fe^{52}	Co^{54}	Ni^{56}
St.	+	St.	+	St.	+	St.

which may be looked for.

$I=1$:

H^3 is β -active, as has been shown by Alvarez and Cornog (1939*b*) changing probably to stable He^3 , and after that we have stable elements up to Cl^{35} in an unbroken series. K^{39} has been shown to be definitely stable. Hence A^{37} ought to be stable, and may be a very rare isotope. Ca^{41} is still unknown, and as it is on the border line, we cannot say whether it will be stable or β^+ -active. From Sc^{43} to Ni^{57} , all are β^+ -active with the exception of Ti^{45} and V^{47} which have to be looked for.

$I=2$:

We have β -active nuclei from H^4 , (rather doubtful) to N^{16} , and then we have alternation of stable and radio-active nuclei beginning from O^{18} . From Sc^{44} , the radioactive

nuclei in this group begin to become β^+ -active and with the exception of Zn^{62} , which may be looked for, we have the group extended up to Ga^{44} .

$I=3$:

In this group, the stable nuclei start from Cl^{37} and end in Ti^{47} . On the left side, they are flanked by β -active nuclei which, with gaps at F^{21} , Na^{25} and P^{33} , can be traced to O^{19} . The group contains the notable anomalous nucleus A^{39} which ought to be stable, but Nier (1936) who specially looked for it states that its abundance is less than 10^{-5} of the most abundant isotope A^{40} . Gregoire (1938*b*) gives it as β -active, but doubtfully. The anomaly ought to be cleared up.

On the right side of the last stable isotope Ti^{47} , the nuclei are all β^+ -active, with the exception of Co^{57} which according to Bleakney *et al* (1936) is stated to be stable with an abundance of .18 per cent. If it is really stable, it forms a glaring anomaly which ought to be cleared up.

The line is continued to Zn^{63} at present, but further β -emitting particles may be discovered on both flanks.

$I=4$:

In this line, as in all with even values of I , the rule of alternation regarding stability is followed, without exception. The limits of the line at present are left S^{36} (stable) and right Ga^{66} (β^+ -active). Co^{58} should be β^+ -active, but the nature of the particles emitted has not yet been ascertained experimentally.

In this and all other groups with *even* values of I , it is still a moot question whether, if the line is extended on both flanks, the nuclei will continue to obey the law of alternation, *e.g.*, whether Si^{32} or Mg^{28} , if discovered, will be stable or β -active. Similarly on the right flank whether Ge^{68} or Se^{72} , if discovered, will be stable or β^+ -active. A third possibility is that like Li^5 , they may be energetically impossible. These remarks apply to the subsequent discussions.

One difficulty in the formation of these 'flank' nuclei would be that of getting any 'starting'-point. This point may be illustrated by a concrete example. Let us take C^{16} and N^{18} which fall in the line $I=4$. Now C^{16} should be stable if rule (1) is obeyed, and N^{18} ought to be β -active. But from what nucleus should we start to get C^{16} ? Since O^{18} is stable, it may be possible to produce N^{18} , but B^{14} will again be difficult to produce.

According to present ideas of stability, all such nuclei may be β -active, but actual experiments can alone decide how far the rule of alternation will extend on both flanks.

As will be seen later, some 'flank' nuclei of the description given here have been obtained in the case of $_{52}\text{Te}$ to $_{58}\text{Ce}$ and $_{35}\text{Br}$ to $_{40}\text{Zr}$ by the fission of the uranium nucleus. But the fission process is probably possible only for the heaviest nuclei.

I=5:

We have in this line 8 stable nuclei from Ti^{49} to Cu^{63} , flanked by β^- -emitting nuclei on the left, and β^+ -emitting nuclei on the right. Sc^{47} may be a stable nucleus or β^- -active. Cl^{39} will be β^- -active.

From I=6, the rules we have stated appear to be followed rigorously. The remarks with respect to 'flank' nuclei are always to be taken subject to the observations made under I=4.

I=6:

Absentees are As^{72} , Br^{76} , both β^+ -active.

I=7:

This line shows only three successive stable isotopes at Cu^{65} , Zn^{67} , Ga^{69} . There are gaps at V^{53} , Cr^{55} , Mn^{57} , Co^{61} (all β^- -active) and at Br^{77} , Kr^{79} , Rb^{81} , Sr^{83} , Zr^{87} and Nb^{89} (all β^+ -active) which may be looked for.

I=8:

This line is very much broken. We have the first stable isotope Ca^{48} , and then after a long pause Ni^{64} . Search may be made for

Sc^{50}	Ti^{52}	V^{54}	Cr^{56}	Mn^{58}	Fe^{60}	Co^{62}	Y^{81}	Zr^{88}	Nb^{90}
—	stable	—	stable	—	stable	—	+	stable	+

Some of these stable isotopes have been looked for by Nier (1938), but have not been obtained. He states that Ti^{52} is $< 10^{-5}$, $\text{Cr}^{56} < 10^{-5}$, $\text{Fe}^{60} < 3 \times 10^{-5}$, $\text{Zr}^{88} < 10^{-5}$, of the respective most abundant isotopes, if they exist at all.

I=9:

We have here stable isotopes from Ga^{71} to Br^{79} . β^+ -active isotopes are expected at Rb^{83} , and Nb^{91} .

I=10:

This series starts with the stable isotope Zn^{70} and is continued up to Cd^{106} . Ru^{98} ought to be stable and we may look for β^+ -active nuclei at Rh^{100} and Ag^{104} .

I=11:

This group contains 11 successive stable isotopes from Br^{81} to Rh^{101} . To this group also belongs Ma^{97} , still undiscovered. The first β^+ -active nucleus is Cd^{107} shown as doubtful. There are two intervening absent nuclei, Pd^{103} and Ag^{105} , which may be β^+ -active. Ga^{73} may be β^- -active.

I=12:

This group starts with the stable nucleus Ge^{76} and is continued up to Sn^{112} . There is one absentee at In^{110} which may be β^+ -active.

I=13:

The stable group starts at Mo^{97} and is continued up to Ag^{107} . Ma^{99} is expected to be stable and one of the chief

isotopes of the element, which is still undiscovered. As^{79} , Y^{81} and Nb^{95} may be β^- -active.

I=14:

This group starts with stable isotope Se^{82} and ends with Sn^{114} . β^- -active isotopes at Br^{84} and Nb^{96} are expected. Besides, a stable Sr^{90} is expected. Nier (1938) looked for the isotope and has found that if it exists its abundance is less than 3×10^{-5} .

I=15:

The first stable nucleus of this group is at Ag^{109} and the last one at Sn^{115} . The nucleus Pd^{107} may be also stable. Br^{85} , Rb^{89} , Sr^{91} , Y^{93} and Nb^{97} may be β^- -active.

Masurium.

The element '43' Masurium has not yet been satisfactorily identified. Let us see what prediction can be made about it. It is expected to have isotopes of the following atomic weights

94	95	96	97	98	99	100	101	102	103
+	+	+—	St.	+—	St.	+—	—	—	—

The two stable isotopes are expected to have the masses 97 and 99. Of these 99 is expected to be more abundant. ${}_{43}\text{Ma}^{99}$, though not yet observed on the earth, has been detected by an indirect method by Abelson (1939b). He observed that Mo^{99} , which is β^- -active (period 64 hrs.), has, besides, a branch activity, and one-fifth of Mo^{99} is converted to ${}_{43}\text{Ma}^{99}$ which emits a γ -ray and lapses to a stable isotope. The γ -ray is internally converted, which expels an electron from the K-shell, and K α -line of Ma is emitted. This has been detected by Abelson.

I=16: (See Chart 2.)

The first stable isotope is at Zr^{96} and the last one so far detected is Xe^{124} . The following radioactive nuclei may be looked for:—

Nb^{93}	Ma^{102}	Rh^{106}	Sb^{118}	I^{122}
—	—	—	+	+

I=17:

There are only three stable nuclei Cd^{113} , In^{115} and Sn^{117} in this group. Sb^{119} is not yet known. It may be either stable or β^+ -active. Ma^{103} and Rh^{107} may be β^- -active.

I=18:

This group starts with Pd^{110} and is continued up to Ba^{130} . Cs^{128} may be β^+ -active.

I=19:

The stable isotopes in this group are Sn^{119} , Sb^{121} and Te^{123} . After these we have neither stable nor radioactive

nuclei in this group. I^{125} may be either stable or β^+ -active; so is Xe^{127} .

$I=20$:

The group starts with the stable nucleus Cd^{116} and is continued up to Sm^{144} . There is a notable absentee amongst stable nuclei at Nd^{140} . Radioactive nuclei are expected at

In^{118}	Cs^{130}	La^{134}	Pr^{138}	$_{61}X^{193}$
—	+ —	+	+	+

$I=21$:

We have got four stable nuclei in this group from Sb^{123} to Xe^{129} . It will be interesting to look for nuclei further beyond at Cs^{131} , Ba^{133} , La^{135} and Ce^{137} . I^{119} may β^- -active.

$I=22$:

The first stable isotope is Sn^{122} and the stable series terminates at the stable isotope Nd^{142} . Radioactive nuclei can be looked for at Cs^{133} , (+ —), La^{136} (+ —).

$I=23$:

The first stable nucleus in this group is Xe^{131} and the last one is Sm^{147} . La^{137} is a notable absentee and Ce^{139} is anomalous. According to our rule this ought to be stable. As a matter of fact cerium shows anomaly in the next group $I=25$ and Ce^{139} as well as Ce^{141} , which are shown to be β^+ - and β^- -active respectively, ought to be stable according to our rule. The gap at $_{61}X^{145}$ is still to be filled up.

$I=24$:

This group shows the first stable nucleus at Sn^{124} and is continued up to Gd^{152} . Sb^{126} ought to be β^- -active. Sm^{148} is α -active. This is indicated by the double arrow which shows that after the emission of α -ray it is transformed into Nd^{144} . According to our classification α -active substances are to be classed with stable nuclei.

$I=25$:

The first stable nucleus is at Ba^{137} and excepting for the anomaly at Ce^{141} this group is continued up to Eu^{151} . Xe^{133} and Cs^{135} may be either stable or β^- -active. Pr^{143} ought to be a stable isotope, so should also be $_{61}X^{147}$. Gd^{153} may be stable or β^+ -active.

$I=26$:

The first stable nucleus is at Te^{130} and the last is at Er^{162} . One may look for the radioactive nuclei at

I^{132}	Cs^{136}	Pr^{144}	$_{61}X^{148}$	Tb^{150}	Ho^{160}
—	—	—	+	+	+

$I=27$:

This contains only two successive stable elements at Eu^{153} and Gd^{155} . The next element Tb^{157} is also probably stable. This group is flanked on both sides by radioactive nuclei which start from Sb^{129} . Search may be made for other radioactive nuclei at

I^{133}	Xe^{135}	Cs^{137}	La^{141}	Ce^{143}	Pr^{145}	$_{61}X^{149}$	Tb^{157}	Ho^{161}	Er^{163}	Tu^{165}
—	—	—	—	—	—	—	+	+	+	+

$I=28$:

This group starts with the stable nucleus Xe^{136} and we should have stable nuclei at Ba^{140} and Ce^{144} . Others, which according to our rule should occur, are present up to Yb^{168} . We should expect the following radioactive nuclei:—

Cs^{138}	La^{142}	Pr^{146}	$_{61}X^{150}$	Ho^{162}	Tu^{166}	Lu^{170} etc.
—	—	—	—	+	+	+

$I=29$:

We have three successive stable nuclei at Gd^{157} , Tb^{159} , Dy^{161} . Eu^{155} and Ho^{163} may be either stable or radioactive. The following radioactive nuclei may be looked for:—

$_{61}X^{151}$	Eu^{155}	Ho^{163}	Tu^{167}	Lu^{171} etc.
—	—	+	+	+

$I=30$:

The group starts with the stable nucleus Nd^{150} and is continued up to Hf^{174} . W^{178} may be a stable isotope of tungsten. The following radioactive nuclei are expected:—

$_{61}X^{152}$	Eu^{156}	Tu^{168}	Lu^{172}	Ta^{176}	Re^{180}
—	—	—	+	+	+

Element 61.

The discovery of element '61' has been claimed and disputed. It is possible to make predictions regarding its number of stable isotopes, their abundance, and radioactive isotopes. The chart shows that we may expect isotopes having the mass-numbers:—

144	145	146	147	148	149	150	151	152
+	St.	+ —	St.	+ —	—	+ —	—	—

The two stable isotopes with $A=145$, 147 will have probably the same order of abundance.

$I=31$:

We have got five successive stable nuclei, viz., Dy^{163} , Ho^{165} , Er^{167} , Tu^{169} , Yb^{171} . They are flanked by a certain number of radioactive nuclei. Search may be made for

$_{61}X^{153}$	Sm^{155}	Eu^{157}	Tb^{161}	Lu^{173}	Hf^{175}	Ta^{177}	W^{179}
—	—	—	— or St. ?	+	+	+	+

I=32:

The series starts with the stable nucleus Gd^{160} and terminates at Os^{184} . Search may be made for the following radioactive nuclei:—

Tb^{162}	Lu^{174}	Ta^{178}	Re^{182}
—	— $\overline{+}$	+	$\overline{+}$

I=33:

We have three successive stable nuclei at Yb^{173} , Lu^{175} and Hf^{177} . Tu^{171} and Ta^{179} may also probably be stable. Search may be made for the following radioactive elements:—

Ho^{167}	W^{181}	Re^{183}	Os^{185} etc.
—	+	+	+

It may be mentioned here, as a proof of the usefulness of the table, that it makes Lu^{175} stable and probably the most abundant isotope. But this nucleus is mentioned as β^- -active in the Tables published by Gregoire (1938*b*). Mattauch and Lichtblau (1939) have subsequently shown that there is an isotope at Lu^{176} with abundance of 2.5% and it has been shown by Libby (1939) that it is Lu^{176} which is β^- -active with the unusually long life of 10^{10} yrs. and not Lu^{175} . Lu^{176} is thus just like long-lived K^{40} and Rb^{87} .

I=34:

This series starts with the stable nucleus Er^{170} and terminates at the stable nucleus Os^{186} . The following radioactive nuclei may be looked for:—

Tu^{172}	Re^{184}
—	— +

I=35:

There are five successive stable isotopes beginning from Hf^{179} up to Os^{187} . They are flanked on the left by two β^- -active nuclei and the following may be looked for:—

Tu^{173}	Lu^{177}	Ir^{189}	Pt^{191}
—	— St. ?	+	+

I=36:

The series starts with the stable isotope Yb^{176} and ends with Hg^{196} . Search may be made for

Lu^{178}	Ir^{190}	Au^{194}	Tl^{198}
—	+	+	$\overline{+}$

I=37:

There are three successive stable nuclei at Re^{187} , Os^{189} and Ir^{191} , flanked as usual on the left by the β^- -active and on the right by β^+ -active nuclei. Search may be made for

Ta^{183}	Au^{195}
—	+

I=38:

This series starts with W^{186} and ends with Hg^{198} . Au^{196} is shown as a β^- -active nucleus with two periods 4 days and 13 hours.

I=39:

This series has four successive stable nuclei from Ir^{193} to Hg^{199} . There may be more stable nuclei to the right *e.g.* at Tl^{201} .

I=40:

This series starts with the stable nucleus Os^{192} and ends with Pb^{204} . Tl^{202} may be β^+ -active.

I=41:

We have two successive stable nuclei, Hg^{201} and Tl^{203} . Pb^{205} may be a stable isotope. On the left side we have the β^- -active nuclei Au^{199} , Pt^{197} and Os^{193} , but on the right side no representative has yet been obtained. We may have Ir^{195} (β^- -active) and Bi^{207} and Po^{209} (β^+ -active).

I=42:

From this series we enter the region of natural radioactivity, the α -emitting nuclei are treated as stable for our purpose. The rule of alternation is obeyed in this series and we have stable nuclei at Pt^{198} , Hg^{202} , Pb^{206} and Po^{210} , the last one being α -active. Au^{200} ought to be β^- -active and Bi^{208} ought to be β^+ -active. These have not yet been found.

I=43:

This series also obeys the laws stated, as we have successive stable isotopes at Tl^{205} , Pb^{207} , Bi^{209} and Po^{211} (α -active). The group is flanked on the left by β^- -active nuclei in which Au^{201} is an absentee. On the right, β^+ -active nuclei may be expected, such as ${}_{85}\text{X}^{213}$ and Rn^{215} .

I=44:

Here also the rule of alternation is followed from Hg^{204} up to Po^{212} (α -active). No β -active nuclei on the left or right have yet been found.

I=45:

We have three β^- -active nuclei and only one 'stable' (α -active) isotope at Bi^{211} . Both Po^{213} and ${}_{85}\text{X}^{215}$ may be either stable or α -active nuclei.

I=46:

Only four isotopes are present which follow the rule, excepting Pb^{210} which is an anomaly. This nucleus is actually β^- -active but ought to be stable or α -active according to our scheme. Rn^{218} may be stable.

I=47:

We have 'stable' nuclei at Po^{215} , Rn^{219} , Ra^{223} and Th^{227} , all being α -active. If the odd number rule is valid then

probably ${}_{85}\text{X}^{217}$, ${}_{87}\text{X}^{221}$ and Ac^{225} should also be 'stable' or α -active.

I=48:

In this series Pb^{212} (Th B) should be stable, but actually it is β -active. Bi^{214} (Ra C) should be β -active but this actually emits, as is well known, both α - and β -rays. Apart from these two anomalies the other nuclei in this series follow the stability rule. These are Po^{216} , Rn^{220} , Ra^{224} and Th^{228} , all being α -active. We should expect ${}_{85}\text{X}^{218}$, ${}_{87}\text{X}^{222}$ and Ac^{226} to be all β -active.

I=49:

This group is very small having only two stable isotopes at Th^{229} (which is doubtful) and Pa^{231} (which is α -active). U^{233} , if it could be obtained, would probably be α -active.

I=50:

Here also we have an exception to the rule in Pb^{214} (Ra B). It ought to emit α -particle, but actually it emits β -rays passing to Ra C. Other nuclei follow the rule. These are Po^{218} , Rn^{222} , Ra^{226} , Th^{230} and U^{234} , all being α -active. We ought to have β -active nuclei at Bi^{216} , ${}_{85}\text{X}^{220}$ and ${}_{87}\text{X}^{224}$. Ac^{228} is found to be β -active and Pa^{232} may be β -active.

I=51:

There is a single stable nucleus U^{235} flanked by three β -active nuclei on the left. ${}_{93}\text{X}^{237}$, according to these rules, may be 'stable', i.e. α -active. It is now well known that U^{235} forms about 0.7% of the most abundant isotope U^{238} .

I=52:

Here also we start with an anomaly at Ra^{228} which instead of being α -active is β -active. The other two nuclei in this group are Th^{232} which is α -active as it ought to be, and Pa^{234} which is β -active. U^{236} ought to be stable (or α -active). ${}_{93}\text{X}^{238}$ ought to be β -active.

I=53:

There are only three nuclei in this group of which the first two, e.g., Ra^{229} and Th^{233} are β -active and ${}_{93}\text{X}^{239}$ is probably stable or α -active. U^{237} may be either α - or β -active. Ac^{231} and Pa^{235} will probably be β -active.

I=54:

In this group the nucleus Th^{234} is an anomaly, because according to the rules it should be α -active, but actually it is β -active. Pa^{236} ought to be β -active.

Element 85—Radio-Iodine.

Element 85, still undiscovered, is expected to have isotopes of the following mass-numbers:—

212	213	214	215	216	217	218	219	220
—	St. (?)	—	St. (?)	—	St. or α -	— or α -	—	—

The stable isotope of element 85 should have an atomic mass of 217.

Element 87—Radio-Caesium.

This element is expected to have isotopes of the following mass-numbers:—

221	222	223	224
St. or α -	—	—	—

So it appears to have only one stable isotope of mass-number 221.

Fission of Uranium and Thorium

After a certain amount of progress had been made with this paper, we received the September (1939) number of the *Physical Review*, containing a paper by Bohr and Wheeler (1939) on the 'Mechanism of Nuclear Fission'. In this paper, the mechanism of nuclear fission is explained by using a (I)/A- diagram (Fig. 8, p. 445) which is very nearly identical with the one used here. As mentioned already, only a part of the diagram from Br^{98} to Sm^{140} is shown, and no other use is made of it, except to illustrate the mechanism of fission.

As few points regarding fission can be elucidated by means of our chart. It has been now proved that the effect of bombarding U or Th-nuclei with neutrons is probably: (1) to release a number of neutrons; estimates vary from 2 to 6 (see Zinn and Szilard, 1939); (2) to split up the remaining nucleus into almost two equal halves, which leave each other with energy of about 200 Mev. The energy of splitting can be calculated from theoretical considerations of the energy-formation of nuclei, and is found to be in accordance with experimental observations.

In some cases, the products of fission and the products of successive disintegrations have been correctly identified, in other cases all the links have not been satisfactorily traced. We give below in Table I a summary of the results so far obtained by different observers, showing the successive series which have been observed.

The tables have been compiled from recent works, particularly those due to Hahn and his co-workers (1939), and Abelson (1939a). We may add some notes regarding the establishment of each series of successive products, and identification of the mass of the nucleus, which is indicated at the top of each column.

The first series (second column of Table I)

${}_{51}\text{Sb}^{127}$	$\rightarrow \beta^-$	${}_{52}\text{Te}^{127}$	$\rightarrow \beta^-$	${}_{53}\text{I}^{127}$
80h		10h		stable

has been cleared up by Abelson, and its mass, 127, was identified from the observation that a 10h-Te isomer was already discovered by Seaborg, Livingood, and Kennedy (1937).

TABLE I.
Products of Fission of Uranium.

Mass \ Nuclei	127	129	131	133 ?	135 ?	137 ?	139	141 ?	143 ?
$_{50}\text{Sn}$	..	..	..	..	..	..	..	..	..
$_{51}\text{Sb}$	80h	4.2h	..	5m	< 10m	< 10m	..	..	..
$_{52}\text{Te}$	90d 10h	30d 70m	30h 25m	77h	43m	60m	..	..	..
$_{53}\text{I}$	I^{127} stable	18.5h	8d	2.4h	54m	22h	..	..	..
$_{54}\text{Xe}$	..	Xe^{129} stable	Xe^{131} stable	st. or —(?)	—	—	..	15m	..
$_{55}\text{Cs}$	..	..	..	Cs^{133} stable	st. or—	—	6m	33m	..
$_{56}\text{Ba}$	..	..	..	..	Ba^{135} stable	Ba^{137} stable	86m	300h	14m
$_{57}\text{La}$	..	..	..	..	..	..	La^{139} stable	36h	2.5h
$_{58}\text{Ce}$	..	..	..	..	..	..	..	Ce^{141*} stable ?	—
$_{59}\text{Pr}$	..	..	..	..	..	..	..	..	Pr^{143} stable
$_{60}\text{Nd}$	..	..	..	..	..	..	..	..	..

* Vide remarks, page 288

It should terminate with stable I^{127} . The fission nuclei are indicated by the symbol φ in the Chart. The nuclei under mass numbers against which there are query marks have not been shown in the Chart.

The mass of the second series ($A=129$) was identified from the 70m (1 h)-Te discovered by Seaborg *et al.* It should end in Xe^{129} (stable—26%).

The mass of the third series ($A=131$) was identified from the 8d-I, discovered by Seaborg *et al.* It should end in Xe^{131} (stable—2.2%).

The identification of the masses of the three remaining series is far from clear; but they cannot have the even masses, 132, 134, 136, as suggested by Abelson (1939a), for according to our chart (*vide* mass-lines 132, 134, 136), I^{132} , Te^{134} and I^{136} should be stable. One has merely to go up along the mass-lines 132, 134, 136 and it can at once be seen that the points I^{132} , Te^{134} , I^{136} would be stable according to the rules formulated by us.

These three unidentified series should have therefore the odd mass-numbers 133, 135, 137 respectively, but it is of course not possible to say which number refers to which group.

X^{133} -group should end in Cs^{133} , *i.e.* we should have in addition a β -emitting Xe^{133} in this group. There is just a chance that Xe^{133} may be stable.

X^{135} -group should end in Ba^{135} , or Cs^{135} if the latter is stable. In any case, we should have a Xe^{135} , β -emitting.

X^{137} -group should end in Ba^{137} . Hence this group should show a β -emitting Cs^{137} and a β -emitting Xe^{137} .

The end product of X^{139} has been definitely identified by Hahn *et al.* (1939) with La^{139} .

The masses of the other two groups are not yet definite. But they cannot be even for the same reason as in the case of X^{133} , 135 , 137 but odd. They have probably the mass-members 141 and 143.

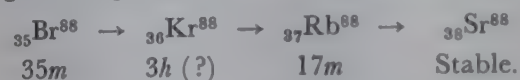
The group X^{141} should end in Ce^{141} , which as remarked already should be a stable isotope of Ce.

The group X^{143} should end in Pr^{143} , *i.e.* it should have β -emitting Ce^{143} .

We have thus shown that according to Hahn *et al.*, and Abelson, one of the immediate products of fission of uranium may be any odd mass from 127 to 143, 9 in number. These contain too large a proportion of neutrons, and therefore undergo successive β -transformations till they end in

stable nuclei which have invariably odd mass numbers. The highest number of β -transformation so far detected is four (for X^{141}).

Since the starting nucleus was either U^{239} or U^{235} , and probably two neutrons are emitted before fission, the other component of fission would be a nucleus with an even mass. For example, the other component of the fission process which gives rise to ${}_{54}X^{143}$ should be ${}_{38}X^{90}$. The results on this side are rather confusing, and the different series have not been completely worked out. Only the following series appear to have been worked out fully:—



This is based on the identification of ${}_{36}\text{Kr}^{88}$, which is, however, doubtful (Langsdorff, 1939).

SUMMARY

A chart has been drawn with A, the mass-number as abscissa, I, the isotope number which is defined as the excess of the number of neutrons over protons as ordinate, and Z-lines, at 45° to the abscissa or ordinate. In this chart, all nuclei, stable as well as radioactive, have been represented with their abundance (for stable nuclei) and half-lives. The chart enables one to form a complete picture of all nuclei so far known, as well as of the nuclear processes. Rules of stability have been noticed; in the case of nuclei with even mass-number, these have been partly foreshadowed by Bethe and Bacher; the rules for stability of odd nuclei which are noted here are believed to be new. A large number of predictions have been made regarding the occurrence of rare stable nuclei, and of radioactive nuclei. In the case of elements still undiscovered, Nos. 43, 61, 85, 87, predictions have been made regarding the number of isotopes and of the most stable varieties. A number of anomalies in the present list of stable elements

have been pointed out which ought to be cleared up. The mass-numbers of the U-fission product series to which Abelson assigned the values 132, 134, 136 have been shown to be untenable. The correct mass-numbers appear to be 131, 133, 135 respectively. Further, two series have been shown to possess the mass-numbers 141 and 143 respectively.

REFERENCES

- ABELSON, 1939*a*, *Phys. Rev.*, **56**, 1.
 ABELSON, 1939*b*, *Phys. Rev.*, **56**, 753.
 ALVAREZ and CORNOG, 1939*a*, *Phys. Rev.*, **56**, 379.
 ALVAREZ and CORNOG, 1939*b*, *Phys. Rev.*, **56**, 613.
 BARTON, 1930, *Phys. Rev.*, **35**, 408.
 BETHE, 1939, *Phys. Rev.*, **55**, 434.
 BETHE and BACHER, 1936, *Rev. Mod. Phys.*, **8**, 82.
 BLEAKNEY, SAMPSON and RIDENOUR, 1936, *Phys. Rev.*, **50**, 382.
 BOHR and WHEELER, 1939, *Phys. Rev.*, **56**, 426.
 BROWN, 1938, *Phys. Rev.*, **53**, 846.
 DELSASSO *et al*, 1939, *Phys. Rev.*, **55**, 113.
 DUBRIDGE *et al* (1937), *Phys. Rev.*, **51**, 995.
 DUBRIDGE *et al* (1938), *Phys. Rev.*, **53**, 447.
 GAMOW, 1934, *Z. f. Phys.*, **89**, 592.
 GAMOW, 1938, *Structure of Atomic Nuclei*. Clarendon Press, Oxford, p. 52.
 GREGOIRE, 1938*a*, *J. de Phys.*, **9**, 419.
 GREGOIRE, 1938*b*, 'Physique Nucleaire'. *Tablettes Annuelles de Constant et Donnees Numeriques*, No. 26.
 GUGGENHEIMER, 1934, *J. de Phys.*, **5**, 253, 475.
 HAHN *et al*, 1939, *Naturwiss.*, **27**, 11, 89, 93, 163, 452, 544.
 HARKINS, 1928, *Z. f. Phys.*, **50**, 97.
 HARKINS, 1931, *Phys. Rev.*, **38**, 1270.
 HEISENBERG, 1932, *Z. f. Phys.*, **77**, 1; **78**, 156.
 HEVESY and LEVI, 1936-37, *Math. fys. Medd., Copenhagen*, **14**, Nr. 5.
 KURIE *et al*, 1936, *Phys. Rev.*, **49**, 468.
 LANGSDORFF, 1939, *Phys. Rev.*, **56**, 205.
 LIBBY, 1939, *Phys. Rev.*, **56**, 21.
 MATTAUCH and LICHTBLAU, 1939, *Z. f. Phys.*, **111**, 514.
 NEWSON, 1937, *Phys. Rev.*, **51**, 620.
 NIER, 1936, *Phys. Rev.*, **50**, 1041.
 NIER, 1938, *Phys. Rev.*, **54**, 275.
 SNELL, 1937, *Phys. Rev.*, **51**, 143.
 ZINN and SZILARD, 1939, *Phys. Rev.*, **56**, 619.

73. ON A PHYSICAL THEORY OF THE SOLAR CORONA

(*Proc. Nat. Inst. Sci. Ind.*, **8**, 99, 1942)

(Received January 14, 1942)

SUMMARY

The paper presents a 'Physical Theory of the Solar Corona' based on the discovery of Grotrian and Edlen that the coronal lines are due to forbidden transitions of atoms of iron, nickel and calcium, stripped of a large number of electrons, and presenting the electron-composition $(3p)^x$ ($x=1$ to 5) for iron and nickel, $(2p)^x$ for calcium. It is shown that such ions can be due to some kind of nuclear reaction only, similar to Uranium Fission, occurring at some depth below the chromosphere and they are not certainly due to large scale meteor flashes. The range and energy balance of such high speed particles (*i.e.* the cross-sections for loss of electrons, and capture of electrons from solar atoms) are calculated and discussed. It is shown that they are in good accord with observed facts. The formation of the outer corona is suggested to be due to the constant stream of δ -rays ejected from the solar atoms by the high speed ions. A programme for further work is indicated.

§ 1. INTRODUCTION

The problem of the solar corona has baffled astronomers and physicists ever since physical science began to be applied for an understanding of its mechanism. The available knowledge, and the different theories up to 1936 are summarised in the *Handbuch der Astrophysik*, Band IV, p. 315, and Band VII, p. 395, and subsequent theoretical attempts are given in the references under the headings Anderson (1926), Minnaert (1930), Grotrian (1931 and 1934), and Thackeray (1940). It will be seen from a perusal of these references that there are two distinct but associated problems involved which may be termed respectively as:—

- (1) The problem of the Coronium.
- (2) The problem of the Corona.

In the Coronium problem, we have to find out the element or elements responsible for the lines 5303, 6374, and others (*vide* Table 1) which are found to occur in the inner corona (from the top layers of the chromosphere up to heights of 5' to 8' from the disc), and which used formerly to be ascribed to a hypothetical element 'Coronium'; and the nature of electronic transition giving rise to these lines.

It is now needless to add that all previous speculations regarding the origin of the coronal lines proved to be wrong. The right clue to identification of the origin of the lines was suggested by Bowen's discovery that the nebular lines can be traced to forbidden transitions of once or multiply ionised light atoms. It was felt that the coronal lines would be found to have a similar origin. The author of the present paper, and probably many others spent considerable time in ransacking the available literature for forbidden lines of elements which may coincide with some of the coronal lines, but without the least success.

The hunt was confined to only singly and doubly, and sometimes trebly ionised atoms, because it was considered improbable that more highly ionised atoms can, without violating ordinary laws of physics, occur in the corona. It was therefore a matter of some surprise when Grotrian, in 1937, announced that the red corona line 6374 had a frequency which was nearly coincident with the frequency difference between the $^2P_{3/2}$ and $^2P_{1/2}$ terms of $Fe^{+9} \dots 3p^5$, which has a chlorine-like structure, and the faint infra-red line 7892 had the frequency corresponding to the difference $^3P_2 - ^3P_1$ of $Fe^{+10} \dots 3p^4$. This identification was not taken very seriously at the time, because we cannot see how, if the laws of physics continue to hold good, we can have iron atoms stripped of as many as nine or ten electrons occurring in the inner corona. But the clue was taken up by Dr. Bengt Edlen (Russell, 1941), and he has succeeded in tracing the most important coronal lines to forbidden transitions of highly stripped medium-weight atoms, viz. to Fe^{+9} , Fe^{+10} , Fe^{+12} and Fe^{+13} possessing $3p^5$, $3p^4$, $3p^2$, $3p^1$ structures; and stripped ions of Ni and Ca having similar structures. Details of this identification, as far as available, are given in Tables 1 and 5. The claim is considered a good one by Prof. H. N. Russell, Dr. D. B. Menzel, and other Harvard astrophysicists. It may be mentioned here that these 'lines' have not been actually produced in the laboratory¹, only their frequencies have been calculated from the term-values obtained from the spectra of highly stripped atoms. The author of the present note along with Mr. D. Kundu has re-examined all the published data, and finds no reason for doubting the identification. It appears therefore almost certain that the problem of the origin of the coronal lines has been finally

¹ In fact none of the nebular lines has yet been actually observed in any laboratory experiment. Only the green auroral line 5577 due to $O \dots 2p^4 \ ^1D_2 - ^1S_0$ has been obtained in the laboratory.

TABLE 1

Lines in the Solar Corona

Wavelength	Frequency	Intensity	Origin	Remarks
3328	30039.46	2.8	..	..
(3359)	29762.24	..	..	..
3388.10	29506.62	44.4	$\text{Fe}^{+12} \dots 3p^3 \text{}^3\text{P}_2 - \text{}^1\text{D}_2$	..
3454.13	28942.59	5.6	..	..
(3461)	28885.14	..	..	..
(3505)	28522.54	..	..	..
(3534)	28288.49	..	..	..
3601.00	27762.17	4.4	$\text{Ni}^{+12} \dots 3p^2 \text{}^3\text{P}_{\frac{1}{2}} - \text{}^3\text{P}_{\frac{1}{2}}$	..
(3626)	27570.76	..	..	..
(3641)	27457.18	..	..	..
3642.9	27442.86	..	..	..
(3648)	27404.50	..	..	..
(3651)	27381.98	..	..	..
3800.8	26302.81	..	..	..
3865	25865.91	..	$\text{Fe}^{+12} \dots 3p^4 \text{}^3\text{P}_1 - \text{}^1\text{D}_2$	Bowen (1940) obtains a line at λ 3871.9, and assigns it to the transition given here.
(3891)	25693.08	..	..	..
3986.9	25075.07	0.8	..	..
4086.3	24465.13	1.2	..	..
(4130)	24206.27	..	..	..
(4131.4)	24298.06	..	..	..
4231.4	23626.21	3.2	..	..
(4244.8)	23551.62	..	..	..
4311.0	23189.97	..	$\text{Ni}^{+11} \dots 3p^5 \text{}^3\text{P}_{\frac{1}{2}} - \text{}^3\text{P}_{\frac{1}{2}}$	(?)
4359.0	22934.61	<0.8	$\text{Co}^{+12} \dots 3p^2 \text{}^3\text{P}_{\frac{1}{2}} - \text{}^3\text{P}_{\frac{1}{2}}$	Identified by D. Kundu (1941).
(4398)	22731.24	..	..	..
(4533.4)	22054.28	..	..	..
4567.0	21890.09	1.2	..	..
4586	21799.40	..	..	..
(4722)	21171.56	..	..	..
(4725)	21158.12	..	..	..
(4779)	20919.04	..	..	..
(5073)	19706.72	..	..	..
5116.03	19540.98	4.8	..	..
5302.86	18852.52	110	$\text{Fe}^{+12} \dots 3p^2 \text{}^3\text{P}_{\frac{1}{2}} - \text{}^3\text{P}_{\frac{1}{2}}$	Discovered in 1868 by Harkness and Young. See further.
5536	18058.58	..	..	..
(5694.0)	17557.48	..	..	..
6374.51	15683.15	28	$\text{Fe}^{+9} \dots 3p^5 \text{}^3\text{P}_{\frac{1}{2}} - \text{}^3\text{P}_{\frac{1}{2}}$	Discovered in 1914. Identification due to Grotrian (1931a).
6704.83	14910.51	3.3	..	Discovered in 1929 by Grotrian (1931a).
7059.6	14161.21	4	..	..
7891.94	12667.68	29	$\text{Fe}^{+10} \dots 3p^4 \text{}^3\text{P}_2 - \text{}^3\text{P}_1$	..
8024.2	12458.88	1.3	..	..
10746.8	9314.4	240	$\text{Fe}^{+12} \dots 3p^3 \text{}^3\text{P}_0 - \text{}^3\text{P}_1$	Discovered by Lyot (1934) by means of the Coronagraph.
10797.9	9261.0	150	$\text{Fe}^{+12} \dots 3p^3 \text{}^3\text{P}_1 - \text{}^3\text{P}_2$	..

NOTE.—The wavelengths are taken from a table given by Dyson and Woolley, *Eclipses of the Sun and the Moon*, p. 132. The intensities are calculated in units of 10^{-6} of the intensity at the same wavelength of photospheric emission, comprised within 1 Å. Lines of doubtful occurrence are given within circular brackets. The identifications as far as they could be inferred from Russell's (1941) short account, and Mr. D. Kundu's investigations are given in column (3). As regards the intensities of the lines, it is well known that they are subject to wide fluctuations. The intensity of the green coronal line 5303 has been found by Lyot (1934) to vary between 3 and 70×10^{-6} of the Fraunhofer spectrum as defined above. The identification of 4359 to $\text{Co}^{+12} - 1s^3 2s^2 2p^0 3s^3 3p^2 \text{}^3\text{P}_{\frac{1}{2}} - \text{}^3\text{P}_{\frac{1}{2}}$ is due to D. Kundu (1942) and should be confirmed. Lines due to forbidden transitions of Fe^{+11} are not in the available range.

solved, and the present paper takes up the study from this point onwards.

§ 2. THE CORONA PROBLEM

The discovery that the 'coronium lines' are due to metastable transitions of very highly stripped heavy atoms considerably enhances the difficulties which have been experienced for the last 80 years in formulating a reasonable physical theory of the 'Solar Envelope'. We use this term in a comprehensive sense after Rosseland (1934), to denote the totality of the phenomena known under the terms: the Reversing Layer, the Chromosphere and the Corona, and consider their problems together as these cannot be dissociated from each other. The composition of the solar envelope is given in Table 2, which is compiled from data given by Unsöld, *Sternatmosphäre* (p. 348). It has not been considered necessary to enter into a critical discussion about the correctness of these values, as the arguments are not likely to be much modified thereby. Full details will be found in Unsöld, *loc. cit.*

TABLE 2

Element	Reversing Layer	Chromosphere	Inner corona
H-atoms ..	1.8×10^{22}	3.6×10^{20}	
O-atoms ..	7×10^{20}		
Metals or C-atoms	7×10^{20}	7×10^{19}	
Free electrons ..	6×10^{20}		7×10^7 per cm. ³ at 1'.

The figures under 'Reversing Layer' represent the total number of atoms over one cm.² of the photosphere. Hydrogen and oxygen are taken to be mostly unionised. The metals or C-atoms of Menzel (1931) are taken to be 80% ionised, and the free electrons are the result of their thermal ionisation. The 'Reversing Layer' may have a depth of 100-150 kilometres, over which we have the chromosphere extending over 10⁴ km. The number of atoms over 1 cm.²

of the base of the 'Chromosphere' (Menzel, 1931) is taken to be roughly 1/1000 of the number in the reversing layer. The inner corona starts from the top of the chromosphere, and show the lines ascribed to 'coronium' usually up to heights of 5', but occasionally in the case of coronal streamers up to heights of 8' to 10' and more. The inner corona also shows a continuous spectrum from which the Fraunhofer lines are absent or blurred out. The outer corona shows a pure continuous spectrum in which the Fraunhofer lines reappear and it extends usually in the quiescent stage up to 15' but in disturbed times, and in the case of streamers up to several solar diameters.

The continuous spectrum in the inner or outer corona was ascribed by Schwarzschild to Rayleigh scattering of photospheric light by free electrons, and subsequent investigations have confirmed it [Grotrian (1934), Minnaert (1930) and Bumbauch (1937)]. The number of free electrons at different heights is calculated by Minnaert (1930) from photometric measurements of the intensity of the continuous coronal light at different heights. The number-density in the quiescent stage is shown in Table 3, but very considerable fluctuations take place occasionally, particularly over coronal streamers.

The Problems of the Solar Chromosphere

The abnormal heights reached by the H, K lines of Ca have been known for a long time to astrophysicists. In recent years quantitative measurements of gradient of density distributions of the different elements have been made by Pannekoek (1928), S. A. Mitchell and E. J. R. Williams (1933), Cillie and Menzel (1935). The figures of the latter are reproduced in Table 4.

The gradients are far smaller than 5.44×10^{-8} cm.⁻¹ ($\alpha = \frac{mg}{kT}$) which is the value for an element of weight unity and for a temperature of 6000°. There appears to be some 'force of levity' in action. The origin of this has been looked for in Selective Radiation Pressure (Milne, 1925), Electrical

TABLE 3

ρ	1	1.03	1.06	1.10	1.2	1.3	1.4	1.6	1.8	2.0
log N	8.66	8.49	8.36	8.19	7.85	7.58	7.38	7.05	6.79	6.57
ρ	2.2	2.4	2.6	2.8	3.0	3.5	4.0	5.0	6.0	8.0
log N	6.40	6.25	6.13	6.04	5.96	5.80	5.71	5.58	5.40	5.21

NOTE : ρ , the distance from the sun's centre is given in units of solar radius. Thus $\rho = 1.03$ denotes 0.48' from the disc, i.e. nearly 2×10^6 km. from the photosphere. The electron density per cm.³ at this point is 3×10^8 . It reduces to $\approx 10^6$ per cm.³ at a distance 7 radii, i.e. 5×10^6 km. The table is taken from Unsöld, *Sternatmosphäre*, p. 440, where it is quoted from a paper by Bumbauch (1937).

TABLE 4

Density-Gradient in the Chromosphere

	Neutral		Ionised		Remarks
H	6563	$1.54 \times 10^{-8} \text{ cm.}^{-1}$	..	..	..
He	5876 $1s 2p^3P - 1s 3d^3D$	0.78	4686	0.30	Vide remarks in text
Mg	..	2.50	4481	—	..
Al	3961, 3944 $3p^2P_{\frac{3}{2}, \frac{1}{2}} - 4s^2S_{\frac{1}{2}}$	2.77	..	—	..
Ca	4227 $4s^2^1S_0 - 4s 4p^1P$	>2.11	3934 $4p^2s_{\frac{1}{2}} - 4p^2P_{\frac{1}{2}}$	1.51	..
Sc	..	—	..	4.20	..
Ti	..	—	..	3.32	..
Cr	..	>2.07	..	1.72	..
Mn	..	2.95	..	1.60	..
Fe	..	2.48	..	1.69	..
Sr	4607 $5s^2^1S_0 - 5s 5p^1P_1$	..	4077, 4215 $5s^2S_{\frac{1}{2}} = 5p^2P$	1.66	..

Force, etc., Turbulence (McCrae, 1929). But what is most disconcerting is the fact that the density gradient appears to have the same value for elements widely differing in weight, e.g. for Mg. (A.W.=24), and Fe (A.W.=58) and is not much larger than that for hydrogen. What 'mysterious forces' reduce the weight of Mg and Ca to almost the same value as that of H is still a problem.

An important constituent of the chromosphere is Helium, which is not observed in the Fraunhofer spectrum but occurs only in the chromosphere as emission lines; though in recent years 10830.3, $1s 2s^3S - 1s 2p^3P$ has been observed by Babcock (1934) as a faint absorption line, and 5876, $1s 2p^3P - 1s 3d^3D$ was observed by Nagaraja Aiyar to occur as an absorption line in the penumbra of spots. As a matter of fact, Evershed (1898) noted that helium lines tended to vanish as we approach the 'Reversing Layer'. Following this Pannekoek and Minnaert (1928) and Perepelkin and Melnikov (1935) have determined the distribution of He-atoms emitting D_3 and 4471 ($1s 2p^3P - 1s 3d^3D$, $1s 2p - 1s 4d^3D$) with height. They observe that the intensity of the lines tend to vanish at the base of the chromosphere, rises to a maximum at a height of 2,500 km. and then gradually vanish, but can be traced up to a height of 7,500 km. Another anomaly discovered by A. Fowler was the occurrence of He+4686, having an excitation potential of 73-volts in the lower chromosphere (2,500 km).

The reversing layer and the chromosphere show plenty

of strong lines of Fe, and Fe^+ and some Fe^{++} -lines have been suspected and the excitation of these lines are satisfactorily explained on the theory of thermal ionisation. But no extranuclear process can deprive the iron atom of thirteen, and possibly of more electrons, at least not in the coronal heights of the sun.

Temperatures of the order of 2×10^7 °C. or photoelectric light of wavelength 1 to 10 Å.U. in sufficient strength would be needed. In fact, Prof. H. N. Russell (1941) remarks:—

'It is hard to see how these stripped atoms can maintain so high a degree of ionisation if the corona, as has generally been supposed, contains many free electrons. But apparent difficulties of this sort often turn out to be guide-posts directing to new knowledge.'

We must add to this that the greatest difficulty has been encountered in finding out a source for these electrons. They cannot arise from thermal or photoelectric ionisation as we have then to postulate, in coronal heights, the existence of atoms and ions; this is impossible on dynamical grounds. Reviewing several theories, Minnaert (1930) remarks: 'Anderson has shown that the corona cannot be in equilibrium if the ordinary physical laws are valid. Instead of assuming, as he does, that very hypothetical modified laws must be applied, we may attempt to account for the corona by assuming that it really is not in equilibrium, and that its particles are continuously projected towards space.'

We shall see later that Minnaert has been right in giving

up the equilibrium theory. We have to find out what forces impel the electrons towards outside space. In fact difficulties of such a serious nature have been encountered in finding out the origin of coronal electrons, that at one time, it was seriously thought that the coronal glow was due to scattering of light quanta by the light quanta themselves. The scattering cross-section for this effect was in fact calculated by Heisenberg and Euler (1934), but was found to have the extremely small value of 10^{-70} cm.² for the average solar radiation. This requires an enormous number of light quanta for the observed effect, and therefore the hypothesis had to be given up.

In addition to the question of origin, the stability of electron clouds in the corona has engaged the attention of physicists, for a cloud of electrons would disperse to nothing in a very short interval of time due to mutual electrostatic repulsion. Anderson at one time pointed out that the presence of an equal number of positrons might ease the situation, but the query about the origin of the hypothetical positrons has never been answered. It is difficult to see how positrons can occur in the corona, for then electrons and positrons would annihilate each other, forming annihilation radiation. There is no indication that such a process ever takes place in the corona.

Another difficulty was pointed out by Moore (1934) and further investigated by Grottrian (1934). Moore showed that though Fraunhofer lines are blurred out from the inner corona, they reappear in the outer corona. Grottrian (1934) found that the continuous spectrum of the scattered radiation from the inner corona shows depressions in regions corresponding to Fraunhofer absorption, but displaced by about 100 Å.U., but the lines appear again in the outer corona. He sought to explain the first of these observations by the hypothesis that electrons in the inner corona are moving outwards with velocities of the order of 4,000 km. (corresponding to a temperature of 4.8×10^5). But for the reappearance of Fraunhofer lines in the outer corona, he had to postulate the existence of 'Cosmic Dust'.

But Astrophysicists have never been able to understand how cosmic dust of the size postulated by Grottrian can exist at such close proximity to the sun without vaporising completely. The phenomena may as well be explained by the hypothesis that the electrons in the outer corona are, at least partly, nearly at rest.

§3. PRELIMINARY EXAMINATION OF DIFFERENT HYPOTHESIS REGARDING ORIGIN OF HIGHLY STRIPPED ATOMS IN THE SOLAR CORONA.

Two suggestions may be made regarding the origin of highly stripped iron and other atoms in the solar corona.

(1) That the production of highly stripped iron, nickel and calcium atoms is due to the bombardment of the solar atmosphere by 'Cosmic Dust' which is meteoric

matter, consisting mainly of elements which occur in great abundance in stony and iron meteorites, viz. Fe, Ni, Ca, Mg, etc. The 'Dust' or 'Meteors' enter the solar atmosphere with a velocity of the order of 6.22×10^7 cm./sec. (velocity of escape from the surface of the sun) which is much larger than 3×10^6 cm., the average velocity of entry of cosmic particle into the Earth's atmosphere. In the case of the meteors it is well known that these get incandescent by friction in the Earth's atmosphere, and give out characteristic lines of neutral and once-ionised atoms of Ca, Fe, Mg, Si (Millmann, 1933) and other elements that they are composed of. In the sun, it may be assumed that on account of the much higher energy, the elements are stripped off of many of their electrons.

According to this view, the coronal lines are due to large scale meteoric flashes, and are caused by the passage of the sun through a cloud of cosmic dust. This hypothesis is examined in § 4 and found to be opposed to facts.

(2) We can assume that the highly ionised iron and other atoms are being constantly produced somewhere in the solar envelope by some kind of *nuclear* reaction, similar to Uranium Fission, or some other type of nuclear reaction still undiscovered, and projected upwards with energies of the order of millions of volts, through the higher chromosphere. The ion may even start as a bare nucleus, and its passage through the higher chromosphere may be compared to that of an α -particle or better of uranium fission fragments through the cloud chamber. During its passage, the Fe-ion goes on capturing and losing electrons, and ejecting electrons from the atoms and ions it encounters (Ionisation by Collision). The capture of electrons by the Fe-ion is illustrated by the emission of the coronal lines and electrons ejected from higher chromospheric atoms and ions probably from the outer corona.

We may call this the δ -ray theory of the origin of coronal electrons. It appears to be in fair agreement with all that we know of the outer corona; the δ -rays, i.e. electrons liberated by the heavy Fe and other ions will have a maximum velocity of twice the amount possessed by the original ions and can therefore rise to four times the height of the ions, and thus we require no heavy ions or atoms for the production of the electron atmosphere which gives rise to the outer corona.

If this view be correct, the solution of the coronium problem has also led to that of the corona problem.

§4. CRITICAL EXAMINATION ON THE METEOR FLASH HYPOTHESIS.

Whether the emitters of Coronal lines are streaming in or streaming out.

Decision may be arrived between the two views by finding out whether the emitters of coronal lines are

streaming out or streaming in. Fortunately, we are in a position to give a definite answer to this point.

Grotian (1931*a*) was the first to find out that the coronal line 5303 has a rather large breadth (of the order of 1 Å.U.). This has been confirmed by Lyot (1934 and 1936) in his Coronagraph observations and he finds for the three most prominent coronal lines the following half-breadths:—

Line.	Half-breadth.	Ratio.
5303	0.80	1.50×10^{-4}
6376	0.97	1.52×10^{-4}
6703	1.07	1.60×10^{-4}

If these breadths are due to Maxwellian motion, the mean velocity is 32 km. per second. Lyot was under the impression that the lines were due to oxygen and he deduced that this signified a temperature of 6.6×10^6 degrees C. Taking the emitters to be iron-ions, the temperature ought to be 2.34×10^6 degrees. Such temperatures are of course unthinkable on the surface of the sun, and Waldemeier (1938) has shown that the width curve of Lyot can be explained on the supposition that the emitters of coronal lines are streaming radially outwards with a mean velocity of 60 km. per sec. Lyot (1934, see Fig. 5) has further found that the width is largest when the emitters are nearest the sun's limb, and becomes narrower as the height increases. This combined with Waldemeier's suggestion points out that the velocity of atoms emitting coronal lines increases inwards, i.e. towards the solar limb.

Let us now try to interpret these facts. Waldemeier's suggestion is quite in agreement with Minnaert's quoted above (page 296, right column, line 26). Further, though his conclusions hold equally well whether the emitters are streaming in or streaming out, the fact that they have a mean velocity of the order of 60 km. per sec. in the inner corona shows that they cannot arise from the ionisation of meteoric matter coming from space. In that case the velocity of entry would be of the order of 600 km./sec. It may be supposed that this velocity diminishes in the inner corona to 60 km. on account of the resistance, but this is not very probable, because, the resisting force would be working far more strongly as the particles plunge inwards, and the velocity would therefore diminish inwards. This is irreconcilable with Lyot's finding that the velocity of the emitters is largest nearest the sun's limb, and diminish outwards.

Russell (1929) considered the dynamics and physical state of meteoric matter near the stars, particularly the sun. His conclusion may be quoted:

'Masses of stone or iron will be completely volatilised by the sun's heat, before they reach the surface, unless they were originally a foot or more in diameter. But the atoms resulting from volatilisation will proceed with unaltered speed, and fall into the sun unless repelled by radiation pressure. . . . Further, the meteoric matter falling into the

sun may scatter enough to account for a small fraction of brightness of the corona, but cannot exert enough effective absorption in the spectrum to produce the equivalent of a single narrow Fraunhofer line' (equivalent width 10^{-3} Å.U.).

It can be easily seen that an iron-atom moving through the sun's atmosphere with a velocity of 6×10^2 km./sec. cannot lose any electron by collision with the free electrons of the upper corona, for the effect is the same as if the iron-atom was at rest, and the electrons were moving past it with a velocity of 6×10^2 km./sec. For an electron, the equivalent energy is merely one-electron volt and is too low to cause even the loss of a single electron from the Fe-atom. It would be otherwise in case of collision with protons, or heavier nuclei (say α -particle or heavier ions). In the case of encounter with protons, it is equivalent to bombarding the iron-atoms with protons of about 2,000 volt energy, and about 13 collisions are sufficient to relieve the iron-atom of 13 electrons. But neither hydrogen lines nor lines of any other familiar elements have been observed beyond a height of 14,000 km. (top of the chromosphere), and as Anderson (1930-1932) has shown it is dynamically not possible that any atom or ion can, under the usual conditions prevailing in the sun, rise to the height of the inner corona (i.e. from the top of the chromosphere to a height of 3' to 5', i.e. 1.30×10^5 to 2.17×10^5 km.). It is therefore almost certain that an iron-atom vaporised from a meteor striking the sun with the usual velocity cannot be relieved of as many as 13 or 14 electrons while passing to the inner corona. We must look for the origin of these highly stripped atoms elsewhere.

§ 5. NUCLEAR REACTION THEORY OF CORONAL EXCITATION.

We shall now develop the ideas of nuclear reaction theory of coronal excitation briefly sketched in § 3. It may be mentioned here that there is already a certain volume of opinion in favour of such a view. Thus Rosseland (1933), after reviewing at length the numerous anomalous results in the solar envelope, points out that some of these anomalies may be explained, by assuming that some kind of radioactive process is in action, *which forces charged particles radially outwards through the envelope*. Naturally enough, no attempt was made to define the nature of this radioactive process, and the reaction of the charged particles with the atoms and ions on the solar envelope.

From the evidence so far available, forbidden lines of Fe^{+9} . . . Fe^{+13} , having the constitution $2p^x$ ($x=5$ to 1), and lines of Ca and Ni having similar constitution have been identified in the corona. It is quite possible that there may be still more highly charged Fe^{+} -ions, viz. Fe^{+14} ($3s^2$), Fe^{+15} (. . . $3s$), Fe^{+16} ($2p^6$). But as these have no metastable levels, there are no means of detecting their

presence in the corona. Fe^{+17} ($2p^5$) does not appear to have been yet spectroscopically investigated, but on extrapolation from known data, the forbidden line $^2P_{3/2} - ^2P_{1/2}$ is expected to have a wavelength of 900 Å.U. This being in a region not available to observation the presence of Fe^{+17} cannot be detected. It can be proved that no other ion of higher charge can emit a metastable line within visible range; hence even if they are present in the corona or lower, in the solar envelope, it is not possible for us to detect their presence.

We shall now give certain arguments which appear to point out that the probability of occurrence of ions more highly stripped than Fe^{+16} or Ni^{+18} is extremely small. For this purpose, we refer the reader to Table 5, in which the ionisation potentials of iron, as far as available, are given.

A glance at Table 5 shows that the ionisation potentials of Fe-ions from Fe^{+8} to Fe^{+16} corresponding to the removal of electrons from $3p$, and $3s$ -shells, vary in continuous gradation from 233 volts to 487 volts. There is a sudden jump at Fe^{+16} ($2p^6$) where the I.P. jumps up to 1250 volts. This is as expected, because now the electron has to be detached for the first time from the $2p$ shell. We calculate the orbital velocities of electrons in the different shells on the assumption that $V = \sqrt{\frac{\text{I.P.}}{13.56}} cf$, where c = velocity of light, f = Sommerfeld fine-structure constant, cf = velocity of the electron in the H-atom. We find (*vide* column 5 of Table 5) that z_i/n varies from 4.15 for Fe^{+8} . $3p^6$ to 5.99 for Fe^{+15} . $3s$ in a continuous sequence, but suddenly jumps to 9.65 cf for the next ion Fe^{+16} .

TABLE 5.

Stripped Iron-ions and their Electron-Structure, etc.

Ion	Electron Structure	Fundamental State	Value of the lowest terms in volts	$\sqrt{\frac{\text{I.P.}}{13.54}} = \frac{z_i}{n}$	Remarks
Fe^{26}I	.. $3d^6 4s^2$	5D_4	7.83	0.76	..
Fe II	.. $3d^6 4s$	$^6D_{4\frac{1}{2}}$	16.5	1.10	Forbidden lines found in η -Carina. Bowen (1936)
Fe III	.. $3d^6$	5D	30.48	1.50	..
Fe IV	.. $3d^5$	6S	56.8	2.05	..
Fe V	.. $3d^4$	5D_0	..	(2.37)*	Bowen (1940) gives metastable lines found in nebulae. D. Kundu thinks that some of these lines may occur in the corona.
Fe VI	.. $3d^3$	$^4F_{3\frac{1}{2}}$	..	(2.69)	"
Fe VII	.. $3d^2$	3F	..	(3.01)	"
Fe VIII	.. $3d$	3D	150.4	3.33	$^3D_{3/2} - ^3D_{5/2} = 1875 \text{ cm.}^{-1}$ No metastable line available.
Fe IX	.. $3p^6$	1S_0	233.5	4.15	No metastable state.
Fe X	.. $3p^5$	2P	261	4.39	$\lambda 6374.75$ $^2P_{3/2} \leftarrow ^2P_{1/2}$
Fe XI	.. $3p^4$	3P	288.9	4.62	$\lambda 7892$
Fe XII	.. $3p^3$	4S	320	(4.91)	Has no metastable line in the available range.
Fe XIII	.. $3p^2$	$^3P_{012}$	346	(5.06)	$\left. \begin{array}{l} 10746.80 \\ 10797.95 \end{array} \right\}$
Fe XIV	.. $3p$	2P	373	5.25	$\lambda 5303$ $^2P_{1/2} - ^2P_{3/2}$
Fe XV	.. $3s^2$	1S_0	454	5.79	No metastable state.
Fe XVI	.. $3s$	$^2S_{1/2}$	487	5.99	"
Fe XVII	.. $2p^6$	1S_0	1259.7	9.65	"

*Parentheses () denote that the value is extrapolated.

In a Uranium Fission process the fragments are formed with energies of the order of 80 to 100 mev. (mev=million-electron-volts). Elements like Fe and Ni can be formed only in a threefold or fourfold fission process, of heaviest elements U^{239} , U^{235} , Prot. Act.²³¹, or Th^{232} , which alone, according to Bohr and Wheeler (1939) are capable of fission. These processes, however, have not yet been observed, but are quite possible on energetic grounds.

If an iron-atom is formed in such a process, its kinetic energy will be of the order 60 mev., corresponding to a velocity of 6.4 cf. If the velocity is 10 cf the energy would be 140 mev., which is impossible on energetic grounds. Let us now ask what will be the number of electrons which will be retained by the fission-fragment? Now Bohr (1940, 1941), Knipp and Teller (1941), and Lamb (1941) have discussed this point in connection with the problem of finding out the net charge carried by a fission-fragment and have shown that the number of electrons retained is limited by the condition that the orbital velocity of the outermost electrons retained by the ion, i.e. V_i should be larger than that of the fragment as a whole, viz. V_f where $\frac{1}{2}M.V_i^2$ =energy of fission. This points out that the fission fragment can be at most Fe^{+15} , but not Fe^{+16} . As Fe^{+15} . $3s$, and Fe^{+14} . $3p^6$ have no metastable levels, they cannot be detected. We can detect ions ranging from Fe^{+13} . $2p$ to Fe^{+9} . $2p^5$, as already noted by Russell (1941).

§6. PASSAGE OF HIGHLY CHARGED (STRIPPED) IONS THROUGH THE SOLAR ENVELOPE.

In this section, the passage of highly charged iron-ions through the solar envelope will be considered. To start with, we do not make any *a priori* assumption regarding the exact point where the stripped ions originate, but merely assume that it happens somewhere in the reversing layer. As a first approximation we consider the envelope to consist mainly of H-atoms, in accordance with considerations given in § 2.

The various possible reactions of a highly stripped iron atom with H-atoms in the solar envelope are:

(1) That the Fe-ions, etc., release electrons from the H-atom by the process known as ionisation by collision [Thomson (1930), Bohr, Bethe (1932), Bloch (1933)].

As we shall see presently, this is the main factor for the reduction in energy of the ion.

(2) When the velocity slows down, due to electron-capture, there may be liberation of the proton (nuclear process).

The loss due to this effect is usually of the order of 10^{-3} times the first, but may be comparable when $V_i \simeq cf$.

(3) The ion may have its charge reduced by capture of free electrons, or electrons from the H-atom.

This process must be taking place in the reversing layer

and the chromosphere, and as a result, the Fe-ion goes on losing its net charge as we actually observe (Fe^{+13} to Fe^{+9}).

Energy loss due to ionisation by collision.

The energy-loss of the Fe-ion due to liberation of an electron from the H-atom is given by Livingstone and Bethe, 1937

$$-\frac{dE}{dx} = \frac{4\pi n e^4 z_i^2}{m V^2} \ln \left(\frac{2m V^2}{I} \right), \quad (1)$$

where E =energy of the particle $=\frac{1}{2}MV^2$,

z_i =effective charge of the ion,

I =average excitation potential of the H-atom.

The effective charge of the Fe-ion varies from $z_i=6$ for Fe^{+15} to $z_i=4$ for Fe^{+8} . We shall, in the first instance, assume z_i to have the average value 5.

The quantity I is not the Ionisation Potential $\frac{2\pi^2 e^4 m}{h^2} = I_0$,

but is $=\gamma I_0$, for particles are usually released with some velocity. The value of γ has been found experimentally for N_2 , O_2 , H, A (Lehmann, 1927), but naturally no experiment can be carried out for H. We have taken $\gamma=2$, and $\gamma=1.2$ rather arbitrarily.

After some work, the formula (1) can be put in the form

$$-\frac{dE}{dx} = n \cdot \sigma_e \cdot mc^2, \quad (2)$$

where σ_e may be called 'the electron-release cross-section' and is given by

$$\sigma_e = 2\pi r_0^2 z_i^2 \left(\frac{Mc^2}{E} \right) \left\{ \ln E + \ln \left(\frac{4m}{MyI_0} \right) \right\}, \quad (3)$$

where $r_0 = \frac{e^2}{mc^2}$ =nuclear radius.

Expressed in electron-volts, we have

$$\sigma_e \cdot mc^2 = 8.37 \cdot 10^{-7} \cdot \frac{\log E - 5.858}{E} \cdot \text{ev. cm.}^2 \quad (3a)$$

In using this formula, E should be expressed in electron-volts. A plot of $\log \sigma_e$ against $\log E$ is given in Fig. 1.

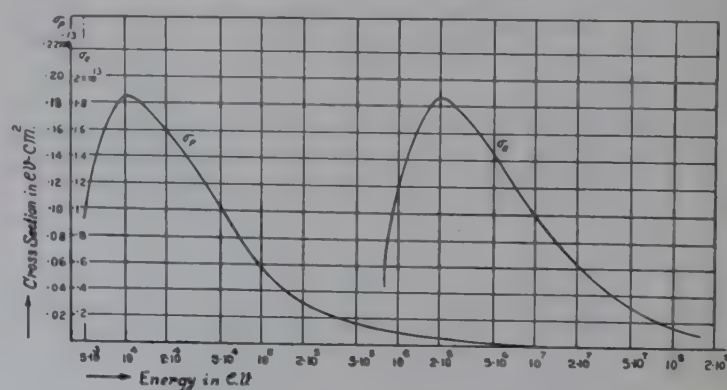


FIG. 1 Electron-release cross-section (σ_e) and proton-release cross-section (σ_p) of a stripped iron atom at different energies ($z_i=5$, $\gamma=2$).

Energy-loss due to proton-release.

Let us next find out the energy-loss suffered by the ion due to communication of energy to the proton. According to Bohr (1940) this is given by:—

$$-\frac{dE}{dx} = n \cdot \sigma_p \cdot mc^2, \quad \dots \quad (4)$$

where σ_p = proton-release cross-section and is given by:—

$$\sigma_p \cdot mc^2 = \frac{4\pi e^4 z_1^2 z_2^2}{M_2 V^2} \cdot \ln \left(\frac{M_1 M_2}{M_1 + M_2} \cdot \frac{V^2 \cdot a_{12}}{z_1 z_2 e^2} \right), \quad \dots \quad (5)$$

where z_1 .. Charge of the ionising particle; here z_i .

z_2 .. ,, ,, ,, nucleus of atom; here = 1.

M_1 .. Mass of the particle, i.e. of Fe-ion.

M_2 .. ,, ,, ,, atom; here M_H

a_{12} .. Effective radius of collision.

Since $M_2 = M_H$ (mass of proton), and $M_1 = 58 M_H$, we can put

$$\frac{M_1 M_2}{M_1 + M_2} = M_3 = M_H.$$

$$a_{12} \simeq a_b \left(\text{Bohr-radius} = \frac{h^2}{4\pi^2 e^2 m} \right).$$

After some work, it can be shown that

$$\sigma_p = 2\pi r_0^2 \frac{m}{M_H} \cdot z_i^2 \left(\frac{Mc^2}{E} \right) \left[\ln E + \ln \left(\frac{M_H}{M z_i I_0} \right) \right]. \quad \dots \quad (6)$$

In deducing this formula, we have made use of the relation $e^2/a_b = 2I_0$.

Expressed in electron-volts, the expression reduces to

$$\sigma_p \cdot mc^2 = 4.56 \times 10^{-10} \left\{ \frac{\log E - 3.594}{E} \right\} \text{ ev. cm.}^2 \quad (6a)$$

A plot of $\log(\sigma_p \cdot mc^2)$ against $\log E$ is shown in Fig. 1.

It is easily seen that σ_p is about $\frac{1}{2000} \sigma_e$, at high values of E ,

but the two become comparable when $E \simeq 10^6$ ev.

We have in fact

$$\frac{\sigma_e}{\sigma_p} = \frac{m_H}{m} \left(\frac{\log E - 5.858}{\log E - 3.594} \right).$$

Formula (3a) is inapplicable when E is $< 10^6$ ev. We have then $V_i \simeq 0.8$ cf, i.e. Fe-ion will by this time acquire electrons, the value of z_i would go down, and formula (3a) ceases to apply.

Depth of the Layer which can be penetrated by the Fe-ion.

We shall now calculate 'the Range' of the highly stripped ions in the solar envelope. The results of the calculation are rendered somewhat uncertain by the fact that we have to choose z and y rather arbitrarily. But this is unavoidable at the present stage.

Following a procedure adopted by P.C. Bhattacharyya (1941), (1) can be put in the form

$$n dx = - \frac{My^2}{128\pi m z_i^2} \cdot \frac{1}{a_b^2} \cdot \frac{d\epsilon}{\ln \epsilon}. \quad \dots \quad (7)$$

where a_b = Bhor-radius = $\frac{h^2}{4\pi^2 e^2 m}$, $\epsilon = \left(\frac{4m}{M} \cdot \frac{E}{y I_0} \right)^2$.

We can as a preliminary measure neglect the other causes of energy loss. These are: losses due to proton release, to gravity, and to collisions with other atoms, viz. Oxygen and C-atoms. We take $z_i = 5$, $y = 2$; we can then apply (7) to find out the number of H-atoms which the Fe⁺-ion can traverse before it loses its energy. We obtain

$$\begin{aligned} \int n dx &= N(x_0) - N(x) = \frac{My^2}{128\pi m z_i^2} \cdot \frac{1}{a_b^2} \int_{\epsilon_0}^{\epsilon_{max}} \frac{d\epsilon}{\ln \epsilon} \\ &= 1.46 \times 10^{18} [E_i(\log \epsilon_m) - E_i(\log \epsilon_0)] \end{aligned} \quad (8)$$

For $E_m = 60$ mev., $\epsilon_{max} = (83.26)^2$, $\log \epsilon_m = 8.833$, $E_i(\log \epsilon_m) = 900$ in round numbers.

Let us take the lower limit $E_0 = 1$ mev., corresponding to $V_i = 2 \times 10^8$ cm./sec. $\simeq$ cf. At this stage, the Fe-ion will have captured electrons from the H-atom, and would have most of its charge neutralized. $E_i(\log \epsilon_0) = 0$, i.e. the formula (8), is inapplicable at this stage.

We find that with these assumptions

$$N = \int n dx = 1.3 \times 10^{21}, \quad \dots \quad (9)$$

i.e. an Fe⁺-ion of net charge $z_i = 5$ and having an initial energy of 60 mev. can pass through 1.3×10^{21} H-atoms before it loses the whole of its energy by electron-release. A reference to Table 2 shows that this is 1/15 of the number of H-atoms over the photosphere. Hence the Fe-ion has to originate rather high up in the reversing layer, but far below the base of the chromosphere. If the Fe-ion has to originate on the photosphere, a rough calculation shows that E_m should be 280 ev., and $V_i = 13$ cf and the iron-ion should be Fe⁺²², ... $1s^2. 2s^2$.

The probable value of 'y' in the case of different gases has been considered by Rutherford, Chadwick and Ellis (*Radiations for Radioactive Substances*, p. 81, Table). For diatomic gases the experimental value of $y = 2$, and for monatomic gases, we have for He, $y = 1.13$, for Ne, A, Kr, $y = 1.3, 1.6, 1.75$, respectively. Atomic hydrogen resembles He most, as it has the smallest number of electrons next to He, and its radiation potential is high like He. A value of $y = 1.12$ is likely therefore to be more correct for H-atoms.

Taking this value of y , we get

$$\sigma_e = 8.37 \times 10^{-7} \frac{\log E - 5.606}{E} \text{ ev. cm.}^2 \quad (10)$$

i.e. the constant is 5.606 instead of 5.858 in formula (3a).

Putting this value of γ in the formula for calculation of range, we find that

$$\int n dz = 4.74 \times 10^{17} [E_i (\log \epsilon_m) - E_i (\log \epsilon_0)]. \quad (11)$$

The value of ϵ 's, however, is different. For $E=60$ mev., $\log \epsilon_m = 9.987$, and $E_i (9.987) \approx 2400$; the value of E_0 , the lowest energy at which the formula ceases to hold now becomes 5×10^5 volts. We have

$$N = 1.12 \times 10^{21} \quad (12)$$

so that the total number of particles which can be traversed remain pretty nearly the same.

The value of z_i varies from 6 to 4. In Fig. 2, the

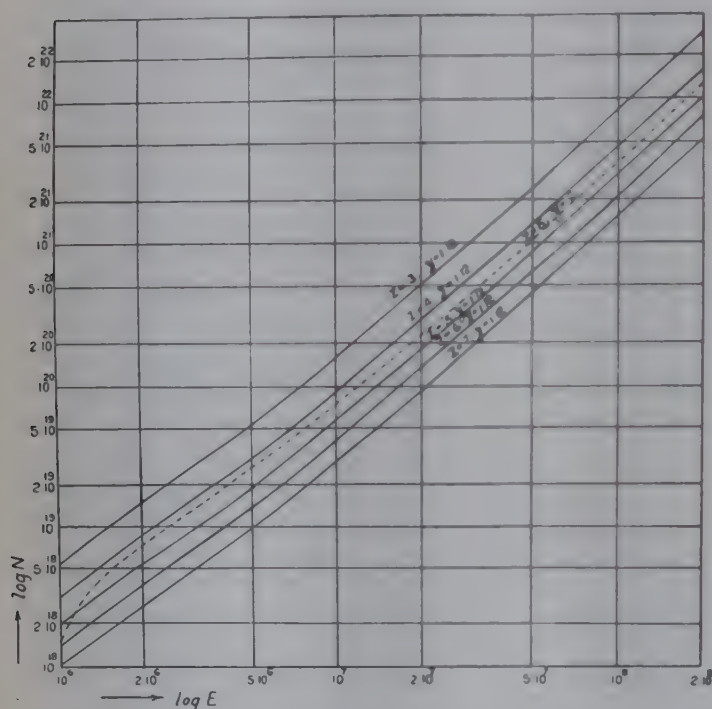


FIG. 2. Total range of a stripped iron atom at different energies for various values of the effective charge. Range has been expressed as the total number of H-atoms traversed.

$\log N / \log E$ curves for different values of z_i , and for $\gamma=1.12$, and for $z_i=5$, $\gamma=2$ are drawn.

§7. CAPTURE AND LOSS OF ELECTRONS BY THE SWIFTLY MOVING IONS.

We have assumed in the foregoing treatment that the iron-ion takes its birth in the reversing layer as an $\text{Fe}^{+16} 1s^2 2s^2 2p^6$ -ion, with an energy of ca 60 mev. and gradually loses this energy on its passage through an atmosphere composed mainly of H-atoms. In course of this passage the ions have a chance of not only capturing free electrons but also electrons from the H-atoms and other atoms and ions; further, it can also lose electrons by collision. Let us now consider this electron exchange phenomena.

The only parallel case in experimental physics is the phenomenon discovered by Henderson (1922) that the α -ray, while passing through the last one cm. of its range in air, can capture an electron from the molecules, and become He^+ , which then might lose an electron by collision. Rutherford showed that this kind of alternate capture and loss takes place nearly two thousand times during the last 1 cm. of the path of the α -particle. Towards the extreme end of the track, He^+ may capture an electron and become neutral He, which may again lose an electron by collision. These cases have been treated by Rutherford (1923) and Jacobsen (1930). A preliminary account may be found in *Radiations from Radioactive Substances* by Rutherford, Chadwick and Ellis (p. 124 *et seq.*).

It has been shown by these authors that if $N(\text{He}^{++})$ be the number of α -particles, $N(\text{He}^+)$ the number of α -particles which have caught an electron, σ_c is the capture cross-section of an electron from air molecules by He^{++} , and σ_l is the loss cross-section of an electron from He^+ , then we have for equilibrium

$$N(\text{He}^{++})\sigma_c = N(\text{He}^+)\sigma_l. \quad \dots \quad (13)$$

In place of σ_c , σ_l , we can introduce λ_c , and λ_l , the mean free-paths for capture, and loss. It is clear that $\lambda_c = \frac{1}{N\sigma_c}$, $\lambda_l = \frac{1}{N\sigma_l}$, where N is the number of air molecules per c.c.

From this relation, we have

$$N(\text{He}^{++})/\lambda_c = N(\text{He}^+)/\lambda_l. \quad \dots \quad (14)$$

λ_l is obtained from experiments, and λ_c from observed ratios of $N(\text{He}^{++})$ to $N(\text{He}^+)$. Kramers and Brinkmann (1930) have developed a theory of capture of electrons from air molecules by the He^{++} -particle, and find that subject to certain assumptions, their results are in agreement with the data given by Rutherford *et al.* Jacobsen (1930) has given a method of calculating λ_l independently.

Let us now turn to the present case. We have supposed that the iron-ion starts its career as an $\text{Fe}^{+16} 1s^2 2s^2 2p^6$ -ion, with a velocity slightly greater than 6 cf. Let us calculate first σ_l for any ion, by following the method given by Jacobsen. We can suppose that the ion is at rest, and the H-atoms are rushing past it with the velocity of the ion, V_i , which is slightly larger than 6 cf. Then an electron can be knocked out of the $\text{Fe}^{+16} 1s^2 2s^2 2p^6$ by either the electron of the H-atom or its nucleus. According to the formula developed by J. J. Thompson (1932), the energy communicated to the electron is given by

$$Q = \frac{2E^2e^2}{mV_i^2(p^2 + d^2)}, \quad \dots \quad (15)$$

where E , M are the charge and mass of the ray (i.e. either the electron, or the nucleus of the H-atom);

e, m are the charge and mass of the electron belonging to Fe^{+16} ;

p = collision distance.

Case (1);

In the first case (ionisation by electron of the H-atom),
 $E=e, M=m$,

$$\therefore Q = \frac{2e^4}{mV_i^2(p^2+d^2)} \text{ and } d = \frac{eE(M+m)}{mMV^2} = \frac{2e^2}{mV^2}.$$

So Q_0 which is the value of Q for $p=0$ and the maximum energy which can be imparted to the electron by the ionising particle equals $\frac{2e^4}{mV^2} \left(\frac{mV^2}{2e^2} \right)^2 = \frac{1}{2}mV^2$.

From (15), we obtain

$$2\pi p dp = -\pi \frac{dp^2}{dQ} dQ = \frac{2\pi e^4}{mV^2} \frac{\delta Q}{Q^2} \quad \dots \quad (16)$$

The total ionising cross-section is obtained by integrating this expression within the limiting values of Q . These are the maximum energy communicated when $p=0$, and W_i , the energy needed to release an electron from the Fe^{+16} -ion. We have then

$$\sigma_i^e = \frac{2\pi e^4}{mV^2} \left[\frac{1}{W_i} - \frac{1}{Q_0} \right] \quad \dots \quad (17)$$

In the case of ionisation by the proton, or any heavy particle it can be shown by a similar procedure that $Q_{\max} = 2mV^2 = 4Q_0$. So we have

$$\sigma_i^p = \frac{2\pi e^4}{mV^2} \left[\frac{1}{W_i} - \frac{1}{4Q_0} \right] \quad \dots \quad (18)$$

So we have

$$\sigma_i = \sigma_i^e + \sigma_i^p = \frac{4\pi e^4}{mV^2} \left[\frac{1}{W_i} - \frac{5}{8Q_0} \right] \quad \dots \quad (19)$$

Now, if we put $V_i = s.c.f$ we have, since $\frac{1}{2} mc^2 f^2 = e^2/a_B$,

$$W_i = z_i^2 \frac{e^2}{2a_B}, \quad Q_0 = \frac{1}{2} mV^2$$

$$\sigma_i = 8\pi a_B^2 \cdot \frac{s^2 - \frac{5}{8} z_i^2}{s^4 z_i^2} \quad \dots \quad (19a)$$

According to Table 2, we have in the solar envelope 90% H-atoms, 3.5% O-atoms, 3.5% C-atoms, and 3% electrons. The O-atoms have each 8 electrons, and each one of these electrons can ionise the Fe^{+} -ion, and similarly some of the electrons of the C-atoms. So the number n of electrons per c.c. which can ionise the Fe^{+} -ion is given by

$$n = n_H + n_O z_1 + n_C z_2 + n_e$$

where n_H, n_O, n_C are the number of H, O and C-atoms.
 n_e = number of free electrons.

Taking $z_1, z_2 = 8$, we have $n = 90 + 8 \times 3.5 + 8 \times 3.5 + 3 = 150$ nearly for 100 solar atoms.

The number of heavy molecules, on the other hand, remain 100. Hence we have

$$\sigma_i = \sigma_i^e + \sigma_i^p = 1.50 \left[\frac{1}{W_i} - \frac{1}{Q_0} \right] + \left[\frac{1}{W_i} - \frac{1}{4Q_0} \right] \\ = 2.50 \left[\frac{1}{W_i} - \frac{0.7}{Q_0} \right].$$

So we have the effective cross-section

$$\frac{\sigma_i}{2.5} = 8\pi a_B^2 \frac{\{s^2 - \alpha z_i^2\}}{s^4 z_i^2} \quad (20)$$

If we multiply this quantity by n , the number of atoms per c.c.

$$\lambda_i = \frac{1}{2.5n\sigma_i} = \frac{1}{20\pi a_B^2} \left(\frac{s^4 z_i^2}{s^2 - \alpha z_i^2} \right) \quad \dots \quad (21)$$

Under the assumptions made here $\alpha = 0.7$, but it can have any value from 0.7 or a somewhat higher value to 0.625 for a purely hydrogen atmosphere.

We have not applied the correction introduced in the ionisation formula by Thomas and E. J. Williams (1933) due to the orbital motion of the electrons as the theory is not yet much developed. The introduction of these corrections may modify the argument substantially.

The value $\log(\sigma/a_B^2)$, for different values of ' s ' and z_i are shown in fig. 3.

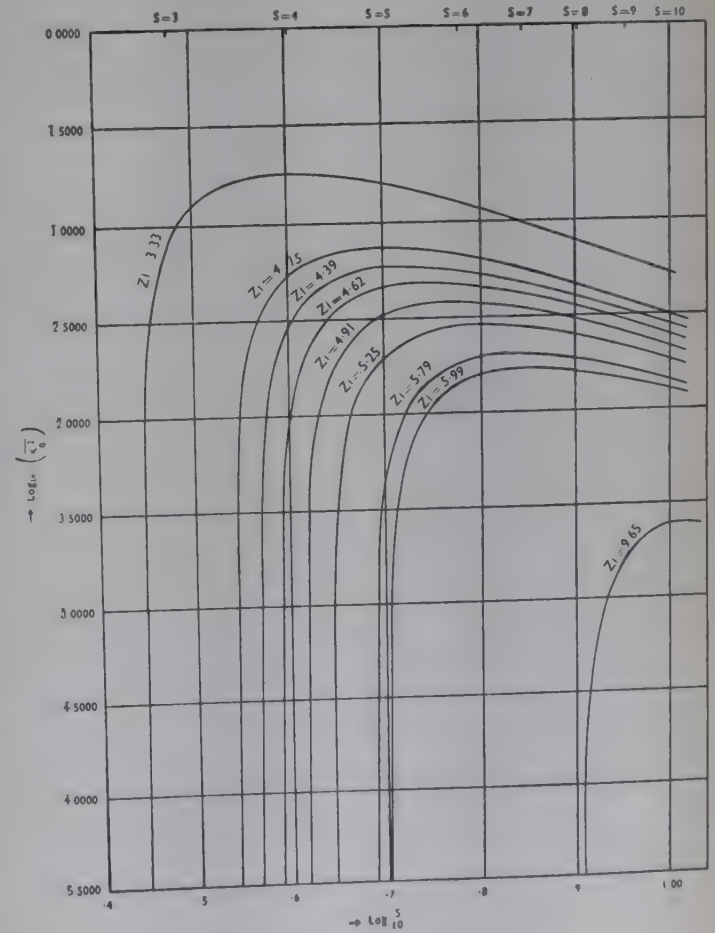


FIG. 3

The general features of these σ_i -curves for the iron-ions may be noted.

We find that there is a critical velocity s_c below which σ_i vanishes. The value of $s_c = \sqrt{\alpha} z_i$. These critical values of velocity and the corresponding energies of the iron-ion are given in the second and third rows of Table 6.

TABLE 6

Fe ⁺	..	16	15	14	13	12	11	10	9	8
s	..	8.072	5.010	4.844	4.392	4.234	4.108	3.865	3.673	3.471
E (in mev.)	..	92.26	35.55	33.22	27.32	25.37	23.89	21.14	19.10	17.06
s_m	..	11.41	7.086	6.850	6.212	5.987	5.809	5.466	5.194	4.909
E (in mev.)	..	184.5	71.09	66.43	54.63	50.75	47.77	42.29	38.19	34.12

The maximum value of σ_i occurs at $s = \sqrt{2\alpha} z_i$, i.e. at $0.99z_i$, i.e. very nearly at $s = z_i$. The value of σ_i (called σ_{lm}) at this point is given by $(\sigma_{lm}/a_0^2) = 7.1\pi/z_i^4$. The value of s_m for the different ions is given in the fourth row of Table 6.

The $\log (\sigma_i/a_0^2) - \log s$ curves are drawn in fig. 3. We note that $\log (\sigma_i/a_0^2)$ rise from $-\infty$ (i.e. $\sigma_i = 0$) at s_c very steeply to the maximum value at $s_m = \sqrt{2} s_c$, and then falls down in a very gentle slope

Electron-capture by the Fe-ions.

In this section, the cross-section for electron-capture by the Fe-ions are calculated. The electron captured may be:—

- (1) a free electron,
- (2) electron bound to the H-atom in the $1s$ -state,
- (3) electron bound to the C-atoms, oxygen and other constituents of the solar envelope.

Capture of Free Electrons.

The problem of capture of free electrons by hydrogen-like ions has been very fully treated by Stobbe (1930). He has given tables of the capture cross-sections of free electrons moving with the velocity ' V ', relative to a stationary hydrogen-like ion with the charge z_i , the capture being effected in the ns, np, nd orbits.

In our present case, the ion is moving through the solar envelope with the velocity $V_i = c.f.s$. The velocity of the electrons relative to the Fe⁺-ion is given by $\vec{V} = \vec{V}_i - \vec{V}_e$, where $\vec{V}_e$ is the velocity of the free electron.

Now $|\vec{V}_i| \gg |\vec{V}_e|$, hence we can put $\vec{V} = \vec{V}_i$ (vide Stobbe's table, p. 687).

Stobbe expresses his capture cross-sections in the form of

functions of a quantity x which in our notation $= \frac{ns}{z_i}$, where n is the total quantum number. With the aid of these tables, we can attempt an estimate of the cross-section for the capture of free electrons by Fe-ions.

For Fe⁺¹⁶. $1s^2 2s^2 2p^6$, we have $z_i/3 = 5.99$, and ' s ' may

be supposed to vary from 6 downwards. We have, therefore, $x = \frac{ns}{z_i} = 1. \dots \dots$ to 0.16, the lower limit being for $s = 1$.

According to Stobbe's tables, $\sigma_{3s}(q_{30}$ in Stobbe's notation) varies from $4.06 \times 10^{-26} \text{ cm.}^2$ to $\approx 5 \times 10^{-21} \text{ cm.}^2$

Since there are probably not more than 6×10^{20} electrons in the solar envelope, we see that the probability of capture of free electrons by the Fe⁺¹⁶-ion is extremely small, except when the velocity has fallen to $V_i \approx cf$. But this takes place in the high chromosphere, where there are not sufficient electrons to capture.

It can be shown in a similar way that the capture cross-section of free electrons by Fe⁺¹⁵. $3s$ is of the same order.

When we come to the Fe-ions, Fe⁺¹⁴ to Fe⁺⁹, the capture takes place in the $3p$ -orbit. As a first step, the problem may be treated as hydrogen-like, the value of $x = \frac{ns}{z_i}$ being obtained

from the known values of (z_i/n) , given in Table 5. The value of q_{3p} is obtained from Stobbe's tables (p. 687), it $= q_{31}$ in his notation. At low velocities, these values are larger than q_{3s} , but at high velocities they are smaller.

For Fe⁺⁹, $z_i/3 = 4.39$, $\frac{ns}{z_i} = 0.228$, $q_{3p} \approx 5 \times 10^{-22} \text{ cm.}^2$ Hence the probability of capture of free electrons by Fe⁺-ions is generally very small.

Case (2).

The general case of electron capture by a swiftly moving ion from any type of ion or atom has not yet been solved. Kramers and Brinkmann (1930) have given a solution of the problem of capture of an electron moving in the s -orbit of some atom by a charged-particle into its own s -orbit, both being regarded hydrogen-like. These results have been applied by them to the data of Rutherford (1923) and Jacobsen (1930) on the capture and loss of electrons by He⁺⁺-particles with good success.

The capture cross-section from one $1s$ -orbit to another s -orbit is given by the formula,²

$$\frac{\sigma}{a_B^2} = \frac{\pi}{5} \cdot 2^{20} \cdot z^5 z'^3 \cdot s^8 / [s^2 + (z+z')^2]^5 [s^2 + (z-z')^2]^5 \dots \quad (22)$$

Here the atom-ion is assumed to have the charge z' , and moves with the velocity $V=cf.s$.

z =charge on the atom from which the electron is captured.

When the capture is from an $1s$ -orbit to an ns -orbit, we have

$$\sigma_n = n^2 \sigma_1(z, z'/n). \quad (23)$$

In the present case, the Fe^{+16} -ion is capturing an electron into the $3s$ -orbit from the H-atom, the electron there being in the $1s$ -orbit. We have put $n=3$, $z'/3=z_i$ of Table 5 = 5.99, $z=1$. Hence we have for Fe^{+16}

$$\frac{\sigma}{a_B^2} = 3^2 \cdot \frac{\pi}{5} \cdot 2^{20} \cdot 5.99^3 \cdot \frac{s^8}{[s^2 + 6.99^2]^5 [s^2 + 4.99^2]^5} \dots \quad (22a)$$

We can apply the same formula for the capture of an electron by the $\text{Fe}^{+15} \dots 1s^2. 2s^2. 2p^6. 3s$ thus completing the $3s^2$ -shell. We have to put $z_i=5.79$. We have then

$$\left(\frac{\sigma_c}{a_B^2}\right) = \frac{3^2 \cdot \pi \cdot 2^{20}}{5} \cdot (5.79)^3 \cdot \frac{s^8}{[s^2 + 6.79^2]^5 [s^2 + 4.79^2]^5} \quad (22b)$$

Values of σ_c for Fe^{+16} and Fe^{+15} different values of ' s ' are given in Table 7.

Electron Balance of the Fe-ions on passage through the Solar envelope.

From the above results on the loss and capture cross-sections of highly ionised atom-ions, we can visualise to some extent the problem of their electron-balance, as they pass through the solar envelope. We assume that the Fe^{+16} -ion is formed with an energy of 60 mev., $V=6.5$ cf. According to (17), the Fe^{+16} can never lose any further electron as this velocity is < 8.06 which is the critical value of s for this ion (*vide* Table 6).

² This formula is different from K. and B.'s No. (4), by the factor $\frac{2^2}{z'^4}$. As K. and B. treat a case where $z'=2$, their calculations remain unchanged.

But the Fe^{+16} -ion can capture an electron, for at this velocity we find from Table 7 that $\sigma_c \simeq 1.4 \times 10^{-20}$ cm.² and the value increases as the velocity falls. The capture takes place after the Fe^{+16} -ion has traversed approximately 7×10^{19} H-atoms, or even less. By this time we calculate from (3a) that the energy falls to $\simeq 58$ mev. and the velocity to $s=6.4$.

Career of the Fe^{+15} -ion.

For the Fe^{+15} -ion, the critical velocity for loss is $s=5.01$ cf. But the Fe^{+15} -ion may start with a velocity of 6.4 cf and σ_i at this point $= 1.3 \times 10^{-18}$ cm.². This is a rather large value, and Fe^{+15} has a chance of losing the electron as soon as it is captured. This may happen, but all this while, the ion goes on losing energy, and the process is repeated, but with lesser chances for loss and increasing chances of capture. So during the stretch $s=6.4$ to $s=5.01$, Fe^{+15} may lose and capture electrons a large number of times till ultimately at $s=5.01$ corresponding to the energy 35.55 mev. σ_i vanishes altogether. The ion, by now, has traversed nearly 4×10^{20} H-atoms (*vide* Fig. 1). There are still about 7×10^{20} H-atoms to traverse.

The Fe^{+14} ion.

From $s=5.01$ to 4.84, $E=35.55$ mev. to 33.22 mev. the Fe^{+14} -ion will have a career similar to that of the Fe^{+15} -ion. The loss cross-section for Fe^{+14} at $s=5.01$ amounts to 1.37×10^{-19} cm.². The capture cross-section cannot be estimated as the capture is now in the $3p$ -orbit. Let us suppose that it is 1/10 that for the $3s$ -orbit for a similar ion, with $s=5.01$. Then we have $\sigma_c \simeq 5 \times 10^{-21}$ cm.² and this varies rather gently with velocity. So at first Fe^{+14} -ion will lose electrons more frequently than it captures but as the velocity falls to $s=4.84$, σ_i vanishes and Fe^{+14} can only capture an electron, and be converted to Fe^{+13} either in the $3p \ ^2P_{\frac{1}{2}}$ or in the $3p \ ^2P_{\frac{3}{2}}$ -state. But on account of the smaller value of σ_c , viz. 5×10^{-21} cm.² the Fe^{+13} -ions have a chance of reaching greater heights, i.e. even a region where H-atoms do not exist, with small velocities. If the capture is in the $3p \ ^2P_{\frac{3}{2}}$ -orbit, conditions are favourable

TABLE 7.

σ_c -Values.

s	8	7	6	5	4	3	2	1
$\log (\sigma_c/a_B^2)$								
Fe^{+16} ..	4.3214	4.5694	4.7632	4.8636	4.8024	4.4584	5.5921	7.5491
Fe^{+15} ..	4.3803	4.6453	4.8621	4.9890	4.9593	4.6483	5.8160	7.7990

for a forbidden transition to $3p\ ^2P_{\frac{1}{2}}$, for the time of flight is nearly 10 seconds, and there are very few electrons or atoms to encounter. Following the general procedure laid down by Condon and Shortley, Pasternack (1940) has calculated the values of transition probabilities of the metastable levels arising from p^x -combinations ($x=1$ to 5). From the values of these transition probabilities and the intensity of the coronal lines, it will be possible to calculate the number of Fe^+ -ions streaming through the solar envelope, and thus forming an estimate of the contribution of this process to the total energy production in the sun. But these considerations are postponed pending calculations of the capture cross-sections in the $3p$ -orbits.

The formation of the other iron-ions with lower net charge, viz. of $\text{Fe}^{+12}\ 3p^2$, $\text{Fe}^{+11}\ 3p^3$, $\text{Fe}^{+10}\ 3p^4$, $\text{Fe}^{+9}\ 3p^5$ takes place according to the same process as is described for Fe^{+13} , by successive capture of electrons, after the velocity of the ion has been reduced by the ionisation-loss to the critical values. A detailed discussion is postponed pending the calculation of p -capture cross-sections.

From this discussion, it appears that Fe^{+13} -ion will be formed usually at a lower level than the succeeding ions, and the Fe^{+9} -ion will be formed at the highest level. But these formation processes all take place in the highest level chromosphere, and the technique is probably not sufficiently advanced to enable astrophysicists to find out the levels where these lines originate.

CONCLUSION

If the considerations presented in this paper be correct, the occurrence of the coronium lines in the solar corona form the first clear fingerpost that nuclear reactions are not confined to the interior of the stars, as already postulated with a certain amount of success by Gamow (1939), and Bethe (1938), and others, but they also take place on the surface of the Sun, and therefore generally on stars as well, and modify in varying degrees the phenomena taking place there. In this connection, the following intuitive remarks of the late Lord Rutherford may be quoted:

'In the furnace of the Sun and other hot stars, the electrons, protons, neutrons, and atoms present must be endowed with high average velocities owing to thermal agitation. It is thus to be expected that the processes both of disintegration and aggregation of nuclei, such as are observed in the laboratory, should be operative on a vast scale for all nuclei, and that a kind of equilibrium should be set up between these two opposing agencies of dissociation and association for each type of atomic nucleus.'

But it is obvious that before we can go to the root of the problems raised by the extraordinary discovery of the origin of coronal lines by Grotrian and Edlen, a large amount of theoretical work and practical observations and work are needed. As the writer of the present paper will not

be in a position to tackle all these problems single-handed, or resume these studies for some time, a brief résumé of some of these problems is given:—

(1) The production of stripped iron and other atoms has been supposed to be due to some kind of nuclear reaction, analogous to Uranium Fission, but the heaviest elements so far discovered on the Sun are Ra^{226} (this is considered doubtful by some). Osmium and Platinum, Uranium and Thorium lines have not so far been discovered, probably because the spectra of these elements have not been so far analysed and classified. It will be a useful task to get the lines of the fission elements classified and look for their occurrence in the Sun.

With respect to the probability of threefold or fourfold fission, fresh experiments are obvious suggestions; if the Fe and Ni-ions responsible for the coronium lines consist of the usual isotopes they should be the end-products of a successive series of α -ray disintegrations, and hence the primary product of fission may be some element with a lesser charge, say ${}_{23}\text{V}^{60}$ or ${}_{24}\text{Cr}^{60}$ but with an extraordinarily large mass, far larger than that of the isotopes of these elements occurring in Nature. This may occur from the fission of the A-products or B-products (Saha, 1941), some of which have very large mass and may therefore possess an inherent instability for fission.

This subject belongs obviously to nuclear physics and has been treated in detail by Bohr and Wheeler (1939), and Flügge (1939).

(2) We require a better knowledge of the composition and density-gradient of the elements in the reversing layer, the chromosphere, and the corona. Our knowledge of the transition layer between the top of the chromosphere ($14''$) and the beginning of the inner corona ($48''$) is particularly defective. Very good work on this line can be done during total solar eclipses, when attempts should be made to photograph fainter coronal lines and prove or disprove their presence. The transitional region may be investigated by means of a powerful Lyot coronagraph at good heights, say at Kodaikanal.

(3) Some progress has been made on the explanation of the peculiarities of the inner and the outer corona on the basis of the δ -ray theory, briefly referred to in § 3, but the matter is so extensive that it can be taken up only in a separate article.

The author expects to return to these and other problems which obviously suggest themselves to an astrophysicist, as soon as circumstances allow him to do so.

It is a great pleasure to record my thanks to my pupils who have taken part in the discussions and helped in the calculations. Mr. D. Kundu has gone through the spectroscopic data as far as available; Messrs. P. C. Bhattacharyya and S. K. Ghosh have checked the calculations and helped in drawing the figures.

REFERENCES.

- ANDERSON, 1926, *Zs. f. Physik*, **37**, 342 (previous references will be found there).
- SABCOCK, 1934, *Proc. Ast. Soc. Pac.*, **46**, 132.
- BETHE, 1932, *Zs. f. Physik*, **76**, 293.
- 1938, *Phys. Rev.*, **54**, 436.
- BHATTACHARYYA, P. C., 1941, *Proc. Nat. Inst. Sci.*, **7**, 275.
- BLOCH, 1933, *Ann. d. Physik*, **16**, 285.
- BOHR AND WHEELER, 1939, *Phys. Rev.*, **56**, 426.
- BOHR, 1940, *Phys. Rev.*, **58**, 650.
- 1941, *Phys. Rev.*, **59**, 270.
- BOWEN, 1936, *Rev. Mod. Phys.*, **8**, 55.
- BOWEN AND WYSE, 1940, *Lick Obs. Bull.*, **19**, 1.
- BUMBAUCH, 1937, *A. N.*, 263.
- CILLIÉ AND MENZEL, 1935, *Harvard Circular*, 410.
- CONDON AND SHORTLEY, *The Theory of Atomic Spectra*.
- FLÜGGE, 1939, *Zs. f. Phys. Chemie*, **B**, **42**, 274.
- GAMOW, 1939, *Phys. Rev.*, **55**, 718.
- GROTRIAN, 1931(a), *Zs. f. Ast. Physik*, **2**, 106.
- 1931(b), *Zs. f. Ast. Physik*, **3**, 199.
- 1933, *Zs. f. Ast. Physik*, **7**, 26.
- 1934, *Zs. f. Ast. Physik*, **8**, 124.
- HENDERSON, 1923, *P.R.S.L. (A)*, **102**, 496.
- HEISENBERG AND EULER, 1934, *Naturwissenschaften*.
- JACOBSEN, 1930, *Phil. Mag.*, **10**, 401.
- KNIPP AND TELLER, 1941, *Phys. Rev.*, **59**, 659.
- KRAMERS AND BRINKMANN, 1930, *Proc. K. A. Amsterdam*, **30**, 973.
- KUNDU, 1942, *Science and Culture*, **7**, 364.
- LAMB JR., 1941, *Phys. Rev.*, **58**, 696.
- LEHMANN, 1927, *P.R.S.L. (A)*, **115**, 624.
- LIVINGSTONE AND BETHE, 1937, *Rev. Mod. Phys.*, **9**.
- LYOT, 1934, *Zs. f. Ast. Physik*, **5**, 73.
- 1936, *M.N.R.A.S.*, **99**, 580.
- 1937, *L'Astronomie*, **51**, 203.
- MCCREA, 1929, *M.N.R.A.S.*, **89**, 483.
- 1934, *M.N.R.A.S.*, **95**, 80.
- MENZEL, 1931, *Lick Observatory Bull.*, **17**, 348.
- MILLMANN, 1933, *Pop. Astr.*, **41**, 298.
- MILNE, 1921, *M.N.R.A.S.*, **81**, 375 and onwards.
- MINNAERT, 1930, *Zs. f. Ast. Physik*, **1**, 226.
- MITCHELL AND E. T. R. WILLIAMS, 1933, *Astro. Jour.*, **77**, 197.
- MOORE, 1934, *Proc. Ast. Soc. Pac.*, **46**, 298.
- NAGARAJA AIYYAR, PRINGSHEIM, *Physik der Sonne*.
- PANNEKOCK AND MINNAERT, 1928, *Verh. Akad. Wet. Amsterdam*, **13**.
- PASTERNAK, 1940, *Ast. Phy. Jour.*, **92**, 129.
- PEREPOLKIN AND MELNIKOV, 1935, *Pulkovo Bulletin*, No. 122, 14.
- ROSSELAND, 1933, *Pub. Obs. Univ. Oslo*, No. 5.
- 1934, *Theoretical Astrophysics*, Chap. XIV.
- RUSSELL, 1929, *Astrph. Jour.*, **69**, 49.
- 1929, *Astrph. Jour.*, **70**, 11.
- 1941, *Scien. American*, August.
- Saha, 1941, *Science and Culture*, **7**.
- STOBEE, 1930, *Ann. d. Physik*, **7**, 661.
- THACKERY, 1941, *Report on Solar Physics* (Progress of Physics, Physical Society, London), **7**, 160.
- THOMPSON, J. J., 1932, *Conduction of Electricity through Gases*, p. 97.
- UNSÖLD, *Physik der Sternatmosphäre*, Kap., **17**.
- WALDEMEIER, 1938, *Zs. f. Ast. Physik*, **15**, 44.
- WILLIAMS, 1932, *P.R.S.L. (A)*, **135**, 108.

74. CAPTURE OF ELECTRONS BY POSITIVE IONS WHILE PASSING THROUGH GASES

M. N. SAHA* AND D. BASU

(Ind. Jour. Phys., **19**, 121, 1945.)

This work extends that of Brinkman and Kramers on the capture of electrons by positive ions while passing through gases. Detailed mathematical working is reported, and it is shown that contrary to the opinion of Brinkman and Kramers, the probability of capture of an electron by the α -particle in the $2p$ -orbit from the H-atom becomes much larger than that for the capture in the $1s$ -orbit when the velocity falls below $2(2\pi e^2)/h$. For small velocities, the ratio goes on increasing.

An α -particle passing through a gaseous medium as in a cloud chamber produces a track consisting of ions formed round electrons liberated from the surrounding gas. It was noticed by Henderson (1923) and Rutherford (1930) that towards the end of the track the phenomenon was more complex. They found that when the velocity had slowed down to a value comparable to $2c\alpha$ ($c\alpha$ = the velocity of the outer electron in the normal level of the H-atom in the molecules of the gas through which the α -ray passes) the α -particle might capture an electron and

be converted to He^+ , this might again lose its electron on collision with matter. The phenomenon of alternate loss and capture may occur a large number of times, but ultimately when the particles have sufficiently slowed down, most of them would permanently acquire an electron and be He^+ . As He^+ further passes through the gas, it may capture an electron and become neutral helium. As it has a velocity of the order of 10^7 to 10^8 cm sec.⁻¹ it may again lose an electron by collision with matter. This process of alternate loss and capture may continue for some more distance till the velocity slows down sufficiently and ultimately we get neutral helium atoms.

*Fellow of the Indian Physical Society.

This phenomenon occurs at the last cm. of the path of the α -particle so that the experimental technique for its observation is rather difficult. The work of Rutherford and Henderson was continued on by Jacobsen (1930) who calculated the capture and loss cross-section from his own experimental works in which the motion of α -particles in air and hydrogen was studied; and he tried to compare his results with the theoretical conclusions of the authors mentioned below.

The theoretical study of this phenomenon was started by Fowler (1924), Thomas (1927), Oppenheimer (1928) and Brinkman and Kramers (1930). Fowler and Thomas used entirely classical conceptions and they need not be further considered. The work of Oppenheimer (1928) has been criticised by Brinkman and Kramers (1930) as one not free from objection. The latter authors have carried out by two alternative methods in the calculations for finding out the capture cross-section. They assume that the atoms of the gas through which the α -particles pass are hydrogen-like and the electrons move in $1s$ -orbits, the capture also is assumed to take place in $1s$ -orbits. The results of their calculations are compared with the experimental data of Rutherford and Henderson and of Jacobsen, and on certain assumptions, they are found to be in good agreement. Brinkman and Kramers (1930) have not, however, calculated the general case when the electrons may be moving in any kind of orbit in the atoms composing the gaseous medium and can be captured in any orbit by the α -particles. The restrictions are evidently for the purpose of simplifying the calculations. The laboratory medium mostly consists of nitrogen, oxygen and hydrogen molecules; though it may be possible to represent the motion of their outermost electrons by proper ψ -functions, the calculations with such ψ -functions may be extremely difficult, if not altogether impracticable to carry out. But if we stick to the approximation of Brinkman and Kramers as far as the traversed gaseous molecules are concerned, it is surely feasible to calculate the capture of electrons in orbits higher than $1s$ by α -particles. Brinkman and Kramers have not carried out this calculation because as they remarked correctly that such cross-sections are likely to be small compared with that of capture in $1s$ orbit. They have, however, given an expression for capture cross-section from $1s$ -orbit to ns and *vice versa*.

The question of capture of electrons to higher p , d and f orbits by the α -particle, however, acquires a new importance in view of the recent suggestion (Saha, 1942) that helium lines occurring in the solar atmosphere may originate in this way: The problem of occurrence of helium lines in the sun has been for long a challenge to astro-physicists. It is well-known that none of the He-lines are found in the Fraunhofer absorption spectrum of the sun. This is as expected because at the temperature prevailing in the sun, He can exist only in normal state and as we know the

absorption lines of normal helium are in the region $\lambda 584\text{\AA}$ to $\lambda 500\text{\AA}$, we cannot expect to observe them. The visible lines of He are all due to the excited states and the lowest of these states has $1s\ 2s\ ^3S_1$ an excitation potential of nearly 20.55 volts, which is not possible to have in an atmosphere having a temperature of $6000\text{--}7000^\circ\text{K}$. But when we turn to the spectrum of the chromosphere, we find that the visible lines of neutral helium are extremely strong, even the well-known line of ionised helium $\lambda 4686\text{\AA}$ is found to occur in it. This is rather an unexpected phenomenon, because this line has an excitation potential of nearly 75.25 volts, while the ordinary excitation in the chromosphere is 9 to 14 volts. There are certain other anomalous features in the occurrence of these lines. Evershed first noticed that the intensity of the He-lines appears to vanish near the limb and they are prominent only at some distance. This phenomenon has been more systematically studied by Perepelkin and Melnikov (1935) and Pannekoek and Minnaert (1928); the results obtained by the first mentioned authors on the variation of intensity of well-known D_3 -line of helium is given in fig (1). It is seen that the line tends to vanish at the limb and attains its maximum intensity at a height of 2500 km. and beyond that it tends to vanish, though it can be traced up to 7500 km. The ionised line $\lambda 4686$ occurs in the lower chromosphere up to a height of 2000 km. only. These facts are rather in sharp contradiction to the ionisation theories as we move up in the solar atmosphere.

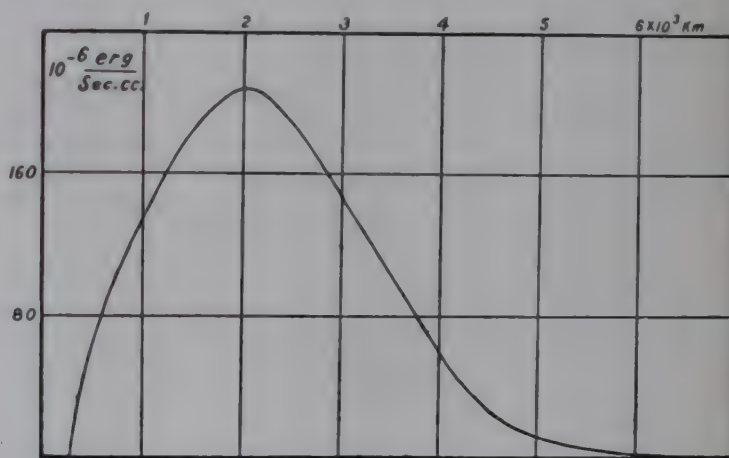


Fig. 1

Emission of 1cc. of Helium chromosphere in D_3 -line in ergs per second and solid angle 4π .

This phenomenon will probably receive a ready explanation if, as already suggested (Saha, 1942), it is assumed that the helium is not an ordinary constituent of the solar atmosphere; it is taken that due to some nuclear process, α -particles are being constantly generated throughout the solar body and some of them quite near the limb. We need not specify the particular nuclear reaction responsible for the generation of the α -particles as we can

make our choice from a host of laboratory experiments. It is well-known that α -particles spontaneously emitted in radioactive disintegration have velocities of the order $6c\alpha$ to $10c\alpha$ (energy 4MV to 10MV).

It is clear that when such α -particles pass through the solar atmosphere, they will, during the first part of the motion, go on ionizing the solar gases (ionisation by collision), and losing energy; when they have sufficiently slowed down, they will begin to capture electrons in different orbits $1s$, $2p$, $3d$, ms , mp , and md . When the electron is captured in any orbit higher than $1s$, we have an excited He^+ -atom which will emit a characteristic spectral line and revert back to a lower state. Most of these lines lie in the extreme ultra-violet, and the only one of He^+ -line available for observation is $\lambda 4686$, $\nu = 4R \left[\frac{1}{3^2} - \frac{1}{4^2} \right]$.

The capture takes place in any one of the $4f$, $4d$ or $4p$, $4s$ orbit and the line is emitted when the electron jumps back to any one of the $3d$, p , s orbits. All other lines of He^+ are outside the limit of experimental observation. This discussion brings out the necessity of calculating the cross-sections for the capture of electrons in orbits higher than $1s$. This has been attempted in the following sections. We have supposed that the solar gas through which the α -particles pass is entirely composed of hydrogen atoms. This very nearly represents the current idea according to which hydrogen forms more than 90% of the solar atmosphere.

When we turn to the next problem of occurrence of He-lines in the solar chromosphere the mathematical difficulties considerably increase. We cannot represent the field of He^+ as even approximately coulombian and hence we must resort to very complicated calculations which have been used by Hylleras (1933, 1937) for finding out the He-terms and their transition probabilities. This has not yet been done, but if time permits it will form the subject of a discussion in another paper.

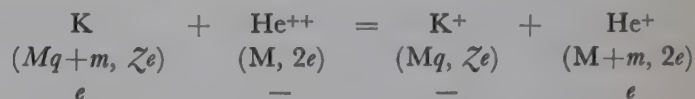
The procedure which we have followed in the calculation of capture of electron from $1s$ - to $2p$ -orbit is similar to the second method as adopted by Brinkman and Kramers in their parallel calculation of $1s$ - to $1s$ -capture. One must bear in mind that the method holds good only when (1) the gaseous molecules of the medium can be regarded as stationary during and after collision and when (2) the velocity of the α -particle is large compared to $c\alpha$.

Obviously these limitations put severe restrictions to the application of the results of the following calculation to solar phenomena. The first limitation means that the molecules or atoms must be very heavy compared to the α -particle; this is far from being the case with hydrogen atoms. The second one has been noted by all workers, but no alternative method has been put forward. It has been suggested that calculations of the Born approximation to second order may be carried out, but in view of

past experience the suggestion does not appear very promising.

In spite of these limitations, we have proceeded with the calculations. In view of the fact that we have followed closely the method of Brinkman and Kramers, it is found useful to rewrite the essential steps of the above authors in the first part of this paper. That will be of help to appreciate the extension we have made of their method.

We suppose that the charged particle (α -particle here) having the mass M and the charge $Z'e$ moves past the atom K which has the mass Mq and the effective charge Ze (without the electron). The type of collision that we propose to study here is the following one: Initially we have an electron moving in the field of the atom, but after collision the same electron is captured by the α -particle in any one of its orbits. The reaction may be schematically represented as follows:



To simplify calculation it is further assumed that Mq is so heavy that its nucleus remains at rest before and after collision.

Let K , α and e represent respectively the atom, the α -particle and the electron which in the beginning of the process belongs to K and at the end is captured by the α -particle. We further choose the direction of motion of the α -particle as the axis of X , the perpendicular from the

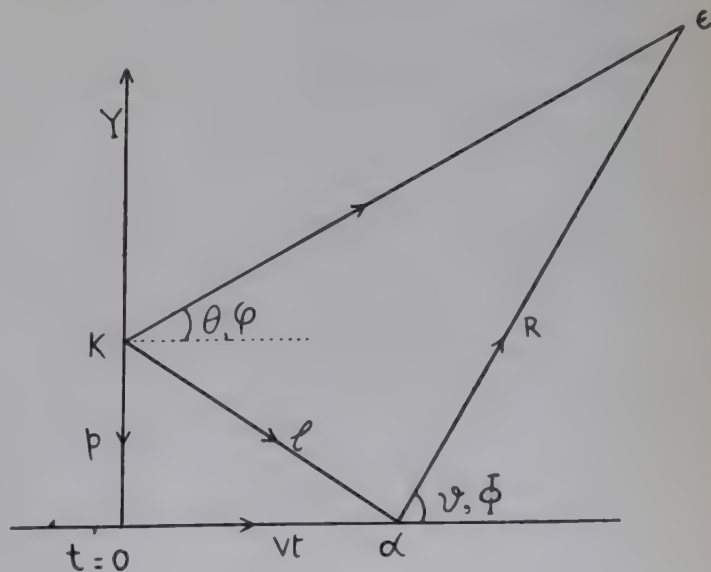


Fig. 2

centre of the atom to the direction of motion as the Y -axis and Z is perpendicular to both. The quantities that will frequently occur are

p , collision parameter.

R , radius vector from α -particle to electron.

r , radius vector from the centre of the atom to electron.

Let us suppose that the α -particle is moving with velocity V , and in time $t=0$, it is at the origin of the co-ordinate system. Then we have at any instant of time

$$\mathbf{R} = \mathbf{r} - \mathbf{p} - \mathbf{V}t \quad (1)$$

The total cross-section for such type of collision is

$$Q = \int_0^\infty 2\pi p |b|^2 dp, \quad (2)$$

where b according to the perturbation theory is given by

$$\frac{h}{2\pi i} \frac{db}{dt} = \int \psi_i \frac{2e^2}{R} \psi_f d\mu. \quad (3)$$

Now ψ_i is the wave function of the electron as attached to the atom in the initial state, while ψ_f is the wave function of the same as attached to the α -particle in the final state. It is easy to see that ψ_f consists of two parts:

$$\psi_f = \psi_{f, orb} \times \psi_{f, tr}$$

where $\psi_{f, orb}$ is the ordinary ψ -function due to the orbital motion of the captured electron round the α -particle and $\psi_{f, tr}$ is due to the translation motion of the electron which it shares because of its being attached to the moving α -particle.

$$\psi_{f, tr} = \exp \left\{ -\frac{2\pi i}{h} \cdot \frac{1}{2} m V^2 t + \frac{2\pi i m}{h} (\mathbf{V} \cdot \mathbf{r}) \right\}.$$

§I

For the case of $1s$ to $1s$ -capture, we have the ψ -functions:

$$\psi_{i, 1s} = \frac{1}{\sqrt{\pi a_z^3}} \exp \left\{ -\frac{r}{a_z} = 2\pi i \nu_0 t \right\} \quad (4a)$$

$$\psi_{f, 1s} = \frac{1}{\sqrt{\pi a_{He}^3}} \exp \left\{ -\frac{R}{a_{He}} - 2\pi i \nu t + \frac{2\pi i}{h} m (\mathbf{V} \cdot \mathbf{r}) - \frac{2\pi i}{h} \frac{m V^2 t}{2} \right\} \quad (4b)$$

where $h\nu_0$ = energy of the electron attached to the atom in the $1s$ -orbit,

$h\nu$ = energy of the same attached to α -particle in the $1s$ -orbit.

$a_z = a/z$, $a_{He} = a/z'$, where a is the Bohr-radius = $\frac{h^2}{4\pi^2 e^2 m}$,

z = charge on atom and z' = charge on α -particle = 2; z' is retained for the sake of uniformity of notation.

Substitution of (4) in (3) gives us:

$$\frac{h}{2\pi i} \frac{db}{dt} = \frac{2e^2}{\pi (a_z a_{He})^{\frac{3}{2}}} \exp \{2\pi i \beta t\} \cdot \int \exp \left\{ -\frac{r}{a_z} - 2\pi i (\sigma_z \cdot \mathbf{r}) - \frac{R}{a_{He}} \right\} d\tau_r d\tau_R, \quad (5)$$

$$\text{where } \beta = \nu - \nu_0 + \frac{m V^2}{2h}, \text{ and } \sigma = \frac{m \mathbf{V}}{h}. \quad (6)$$

To evaluate (5), use has been made of the following Fourier-integral

$$\frac{1}{R} \exp \left\{ -\frac{R}{a} \right\} = 4\pi a^2 \int \frac{\exp \{2\pi i (\mathbf{R} \cdot \mathbf{q})\}}{1 + 4\pi^2 a^2 q^2}, \quad (7)$$

where $\mathbf{q}$ is any arbitrary vector having the dimension of $1/\text{Length}$.

We have

$$(\mathbf{q} \cdot \mathbf{R}) = -q_z V t - q_z p + (\mathbf{q} \cdot \mathbf{r}), \quad (8)$$

then we may rewrite (5) as

$$\begin{aligned} \frac{h}{2\pi i} \frac{db}{dt} &= \frac{8e^2}{(a_z a_{He})^{\frac{3}{2}}} \exp \left\{ 2\pi i V \left(\frac{\beta}{V} - q_z \right) t \right\} \\ &\times \int \frac{\exp \{ -r/a_z + 2\pi i (\mathbf{q} - \sigma, \mathbf{r}) - 2\pi i q_z p \}}{(1/a_{He}^2) + 4\pi^2 q^2} \\ &\quad r^2 dr \sin \theta d\theta d\phi d\mathbf{q}. \end{aligned} \quad (9)$$

Integration with respect to ' t ' gives us the well-known δ -function of Dirac. (*vide*, Dirac, Quantum Mechanics, 1935, p. 72),

$$\begin{aligned} \frac{h}{2\pi i} b &= \frac{8e^2}{(a_z a_{He})^{\frac{3}{2}}} \frac{1}{V} \\ &\int \frac{\delta \{ \beta/V - q_z \} \exp \{ -r/a_z + 2\pi i (q - \sigma) r \cos \theta - 2\pi i q_z p \}}{(1/a_{He}^2) + 4\pi^2 q^2} \\ &\quad \times r^2 dr \sin \theta d\theta d\phi d\mathbf{q}. \end{aligned} \quad (10)$$

The integration with respect to q_z follows from the properties of the δ -function

$$\begin{aligned} \frac{h}{2\pi i} b &= \frac{8e^2}{(a_z^2 a_{He}^3)^{\frac{1}{2}}} \frac{1}{V} \\ &\left\{ \int \frac{\exp \{ -r/a_z + 2\pi i (q - \sigma) r \cos \theta - 2\pi i q_z p \}}{(1/a_{He}^2) + 4\pi^2 q^2} \right. \\ &\quad \left. \times r^2 dr \sin \theta d\theta d\phi d\mathbf{q}_z d\mathbf{q}_z \right\}_{q_z = \beta/V}. \end{aligned} \quad (11)$$

Integrating with respect to θ, ϕ, r , we have

$$\begin{aligned} \frac{h}{2\pi i} b &= \frac{64\pi e^2}{(a_z^5 a_{He}^3)^{\frac{1}{2}}} \frac{1}{V} \\ &\left\{ \int \frac{\exp \{ -2\pi i q_z p \} dq_z d\mathbf{q}_z}{[(1/a_z^2) + 4\pi^2 (q - \sigma)^2]^{\frac{3}{2}} [(1/a_{He}^2) + 4\pi^2 q^2]} \right\}_{q_z = \beta/V}. \end{aligned} \quad (12)$$

From the energy-principle, the two factors in the denominator are equal (*vide* appendix 1). Hence

$$\frac{h}{2\pi i} b = \frac{64\pi e^2}{(a_z^5 a_{He}^3)^{\frac{1}{2}}} \frac{1}{V} \cdot \int \frac{\exp \{ -2\pi i q_z p \} dq_z d\mathbf{q}_z}{[(1/a_{He}^2) + 4\pi^2 \{ (\beta^2/V^2) + q_z^2 + q_z^2 \}]^{\frac{3}{2}}}. \quad (13)$$

$$= \frac{64\pi e^2}{(a_z^5 a_{He}^3)^{\frac{1}{2}}} \frac{1}{V} \frac{3}{16} \int \frac{\exp \{ -iy p \}}{(g^2 + y^2)^{\frac{5}{2}}}, \quad (14)$$

where

$$y = 2\pi qy, \quad g^2 = \frac{1}{a_{\text{Ho}}^2} + \frac{4\pi^2\beta^2}{V^2}$$

or

$$|b| = \frac{2^3 \pi e^2}{(a_s^5 a_{\text{Ho}}^3)^{1/2}} \cdot \frac{1}{hV} \left(\frac{1}{a_{\text{Ho}}^2} + \frac{4\pi^2\beta^2}{V^2} \right)^{-2} x^2 K_2(x), \quad x = pg \quad (15)$$

where $K_\nu(x) = \frac{1}{2}\pi i \exp \frac{\pi\nu i}{2} H_\nu^{(1)}(\exp\{i\pi/2\}x)$,

$H_\nu^{(1)}$ being the Hankel function of the first kind (Copson, 1933). Substituting this value of $|b|$ in (2), we have

$$Q = \frac{2^7 \pi^3 e^4}{(a_s^5 a_{\text{Ho}}^3)^{1/2}} \cdot \frac{1}{h^2 V^2} \left(\frac{1}{a_{\text{Ho}}^2} + \frac{4\pi^2\beta^2}{V^2} \right)^{-5} \int x^5 |K_2(x)|^2 dx \\ = \frac{2^{12} \pi^3}{5(a_s^5 a_{\text{Ho}}^3)} \cdot \frac{e^4}{h^2 V^2} \left(\frac{1}{a_{\text{Ho}}^2} + \frac{4\pi^2\beta^2}{V^2} \right)^{-5} \quad (\text{vide appendix 3}). \quad (16)$$

Replacing the value of β , and after some calculation, we have

$$Q = \frac{2^{12} \pi^3 e^4}{5(a_s^5 a_{\text{Ho}}^3)} \cdot \frac{e^4}{h^2 V^2} \left[\frac{1}{2a_{\text{Ho}}^2} + \frac{1}{a_s^2} + \pi^2 \sigma^2 + \frac{\left(\frac{1}{2a_{\text{Ho}}^2} - \frac{1}{a_s^2} \right)^2}{16\pi^2 \sigma^2} \right]^{-5} \quad (17)$$

Putting $V = c\alpha$ we obtain after some reduction

$$Q = \frac{2^{20} \pi a^2 z^5 z'^3}{5} s^3 \cdot [s^2 + (z - z')^2] \{s^2 + (z - z')^2\}^{-5}. \quad (18)$$

This is the formula given by Brinkman and Kramers for capture from $1s$ to $1s$ -orbits.

§ 2. CAPTURE IN THE $2p$ -ORBIT

Let us now proceed with the calculation of the cross-section for the capture of the electron from $1s$ to $2p$ -orbits. The ψ -function for the initial $1s$ -orbit is the same as before. The ψ -function for the $2p$ -orbit is now triple, corresponding to the magnetic quantum numbers $m=0, \pm 1$. We have

$$\psi_{f, 2p} = \frac{1}{4\sqrt{\pi a_{\text{Ho}}^2}} \cdot \frac{R}{a_{\text{Ho}}} \exp \left\{ -\frac{R}{2a_{\text{Ho}}} - 2\pi i vt - \frac{2\pi i}{h} \cdot \frac{mV^2 t}{2} \right. \\ \left. + \frac{2\pi i m}{h} (\mathbf{V} \cdot \mathbf{r}) \right\} \left\{ \frac{\cos \vartheta}{\sqrt{2}} \right. \\ \left. \frac{\sin \vartheta \exp \{\pm i\phi\}}{2} \right\} \quad \dots \quad (19)$$

The upper one is for $m=0$, the lower for $m=\pm 1$.

Here ϑ, ϕ denote the polar angles of the electron with reference to the α -particle as origin. But in shifting the origin to the nucleus K which, in our approximation, is at rest, the new angles θ and ϕ are connected with ϑ , and ϕ in the following way

$$R \cos \vartheta = (r \cos \theta - Vt), \quad R \sin \vartheta \exp \{\pm i\Phi\} = \\ (r \sin \theta \exp \{\pm i\phi\} - p). \quad (20)$$

The Fourier-integral here takes the form

$$\frac{1}{R} \exp \{-R/2a_{\text{Ho}}\} = 2\pi a_{\text{Ho}}^2 \cdot \int \frac{\exp \{i\pi (\mathbf{q} \cdot \mathbf{R})\}}{1 + 4\pi^2 a_{\text{Ho}}^2 q^2} d\mathbf{q}. \quad (21)$$

We obtain as before

$$\frac{h}{2\pi i} \frac{db}{dt} = \frac{e^2}{4\sqrt{a_s^3 a_{\text{Ho}}^5}} \exp \left\{ 2\pi i V \left(\frac{\beta}{V} - \frac{q_x}{2} \right) t \right\} \\ \int \frac{\exp \left\{ -\frac{r}{a_s} + 2\pi i \left(\frac{q_x}{2} - \sigma \right) r \cos \theta - \pi i p q_y \right\}}{\left\{ \frac{1}{4a_{\text{Ho}}^2} + \pi^2 (q_s^2 + q_y^2 + q_z^2) \right\}} \times \\ \exp \{ \pi i r \sin \theta (q_x \cos \phi + q_z \sin \phi) \} d\mathbf{r} d\mathbf{q} \left\{ \begin{array}{l} (r \cos \theta - Vt) \sqrt{2} \\ (r \sin \theta \exp \{\pm i\phi\} - p)/2. \end{array} \right. \quad (22)$$

Integrating with respect to t , with the aid of Dirac's delta-functions, we have

$$\frac{h}{2\pi i} b_{m=0} = \frac{e^2}{4\sqrt{2a_s^3 a_{\text{Ho}}^5}} \cdot \frac{1}{V} \int \dots d\mathbf{r} d\mathbf{q} F(r, q_x, q_y, q_z) \\ \left\{ r \cos \theta \cdot \delta \left(\frac{q_x}{2} - \frac{\beta}{V} \right) + \frac{1}{2\pi i} \cdot \delta' \left(\frac{q_x}{2} - \frac{\beta}{V} \right) \right\}, \quad (23)$$

where

$$F(r, q_x q_y q_z) \\ \exp \left\{ -\frac{r}{a_s} + 2\pi i \left(\frac{q_x}{2} - \sigma \right) \cdot r \cos \theta - \pi i p q_y + \pi i r \sin \theta \right. \\ \left. (q_y \cos \phi + q_z \sin \phi) \right\} \\ = \frac{1}{4a_{\text{Ho}}^2 + \pi^2 (q_x^2 + q_y^2 + q_z^2)}. \quad (24)$$

Integrating with respect to q_x we have

$$\frac{h}{2\pi i} b_{m=0} = \frac{e^2}{2\sqrt{2a_s^3 a_{\text{Ho}}^5}} \cdot \frac{1}{V} \int \dots \left[F(r, q_x/2 = \beta/V, q_y, q_z) \right. \\ \left. r \cos \theta d\mathbf{r} - \frac{1}{2\pi i} \cdot F'(r, q_x/2 = \beta/V, q_y, q_z) d\mathbf{r} \right] dq_y dq_z. \quad (25)$$

Here F' denotes differentiation of F with respect to $q_x/2$, and the substitution of β/V for $q_x/2$. On simplification

$$b_{m=0} = \frac{4\pi^2 e^2 \beta/V}{hV\sqrt{2a_s^3 a_{\text{Ho}}^5}} \cdot \int \frac{\exp \left\{ -\frac{r}{a_s} + 2\pi i \left(\frac{\beta}{V} - \sigma \right) r \cos \theta \right. \\ \left. - \pi i p q_y \cos (\phi - \chi) \right\}}{\left[\frac{1}{4a_{\text{Ho}}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2 (q_y^2 + q_z^2) \right]} \\ \times r^2 dr \sin \theta d\theta d\phi dq_y dq_z, \quad (26)$$

where

$$c = \pi r \sin \theta \sqrt{q_y^2 + q_z^2} = k \sin \theta. \\ \chi = \tan^{-1}(q_z/q_y).$$

Similarly

$$b_{m=\pm 1} = \frac{i\pi e^2}{2\sqrt{a_z^3 a_{H_0}^5}} \cdot \frac{1}{hV} \int \frac{\exp\left\{-\frac{r}{a_z} + 2\pi i \left(\frac{\beta}{V} - \sigma\right) r \cos \theta - \pi i p q_v\right\}}{\left\{\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right\}} dq_v dq_z$$

$$+ \exp\{i\chi \cos(\phi - \chi)\} \cdot \{r \sin \theta \exp(\pm i\phi) - p\} \cdot r^2 dr \sin \theta d\theta d\phi \quad (27)$$

The integration of (26 & 27) with respect to ϕ , gives us

$$b_{m=0} = \frac{8\pi^3 e^2 \beta / V}{hV \sqrt{2a_z^3 a_{H_0}^5}} \cdot \int \frac{\exp\left\{-\frac{r}{a_z} + 2\pi i \left(\frac{\beta}{V} - \sigma\right) r \cos \theta - \pi i p q_v\right\}}{\left[\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right]^2} J_0(k \sin \theta) \cdot r^2 dr \sin \theta d\theta dq_v dq_z \quad (28)$$

and

$$b_{m=\pm 1} = \frac{i\pi^2}{\sqrt{a_z^3 a_{H_0}^5}} \cdot \frac{e^2}{hV} \int \frac{\exp\left\{-\frac{r}{a_z} - 2\pi i \left(\frac{\beta}{V} - \sigma\right) r \cos \theta - \pi i p q_v\right\}}{\left\{\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right\}} \times r^2 dr \sin \theta d\theta dq_v dq_z \cdot \{r \sin \theta i J_1(k \sin \theta) \exp(+i\chi) - p \cdot J_0(k \sin \theta)\} \quad (29)$$

A similar integration with respect to θ gives us

$$b_{m=0} = \frac{16\pi^3 e^2 \beta / V}{hV \sqrt{2a_z^3 a_{H_0}^5}} \cdot \int \frac{\exp\left\{-\frac{r}{a_z} - \pi i p q_v\right\} \sin nr}{\left[\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right]^2} \cdot \frac{r}{n} dr dq_v dq_z \quad (30)$$

and

$$b_{m=\pm 1} = \frac{2i\pi^2 e^2}{hV} \int \frac{\exp\left\{-\frac{r}{a_z}\right\} \left(\frac{\sin nr}{nr} - \cos nr\right) \frac{im}{n^2} \exp\{-\pi i p q_v\}}{\left\{\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right\}} r^2 dr dq_v dq_z \quad (31)$$

where

$$n = \sqrt{l^2 + m^2}, \quad l = 2\pi \left(\frac{\beta}{V} - \sigma\right), \quad m = \pi \sqrt{q_v^2 + q_z^2}. \quad (32)$$

Integrating with respect to r , we have

$$b_{m=0} = \frac{32\pi^3 e^2 \beta / V}{hV \sqrt{2a_z^3 a_{H_0}^5}} \times \int \frac{\exp\{-\pi i p q_v\} dq_v dq_z}{\left\{\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right\}^2} \left\{\frac{1}{a_z^2} + 4\pi^2 \left(\frac{\beta}{V} - \sigma\right)^2 + \pi^2(q_v^2 + q_z^2)\right\}^2 \quad (33)$$

$$b_{m=1} = \frac{4i\pi^3}{\sqrt{a_z^3 a_{H_0}^5}} \cdot \frac{e^2}{hV} \cdot \int \frac{\exp\{-\pi i p q_v\} dq_v dq_z}{\left\{\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right\}} \times \left\{ \frac{4im \exp\{i\chi\}}{\left[\frac{1}{a_z^2} + 4\pi^2 \left(\frac{\beta}{V} - \sigma\right)^2 + \dots\right]^3} - \frac{p}{\left[\frac{1}{a_z^2} + \dots\right]} \right\}. \quad (34)$$

It is easy to deduce from the law of conservation of energy that the two factors in the denominator are equal; i.e.,

$$\left\{\frac{1}{4a_{H_0}^2} + \frac{4\pi^2 \beta^2}{V^2} + \pi^2(q_v^2 + q_z^2)\right\} = \left\{\frac{1}{a_z^2} + 4\pi^2 \left(\frac{\beta}{V} - \sigma\right)^2 + \pi^2(q_v^2 + q_z^2)\right\}. \quad (35)$$

Making use of this relation, and integrating with respect to q_v and q_z , we have

$$\left. \begin{aligned} b_{m=0} &= \frac{2\pi}{3} \cdot \frac{2\pi\beta/V}{(2a_z^3 a_{H_0}^5)^{1/2}} \cdot \frac{e^2}{hV} g^{-6} x^3 K_3(x) \\ b_{m=1} &= -\frac{i}{3} \cdot \frac{\pi}{(a_z^3 a_{H_0}^5)^{1/2}} \cdot \frac{e^2}{hV} g^{-8} x^3 K_2(x) \end{aligned} \right\}, \quad (36)$$

where

$$g^2 = \left(\frac{1}{4a_{H_0}^2} + 4\pi^2 \frac{\beta^2}{V^2}\right), \quad x = pg.$$

Substituting the above values in expression (2) we obtain

$$\left. \begin{aligned} Q_{m=0} &= \frac{2^2 \cdot \pi^3}{3^2} \cdot \frac{(2\pi\beta/V)^2}{a_z^3 a_{H_0}^5} \cdot \frac{e^4}{h^2 V^2} g^{-14} \int_0^\infty x^7 dx \{K_3(x)\}^2 \\ Q_{m=1} &= \frac{2\pi^3}{3^2 a_z^3 a_{H_0}^5} \cdot \frac{e^4}{h^2 V^2} g^{-12} \int_0^\infty x^7 dx \{K_2(x)\}^2 \end{aligned} \right\}. \quad (37)$$

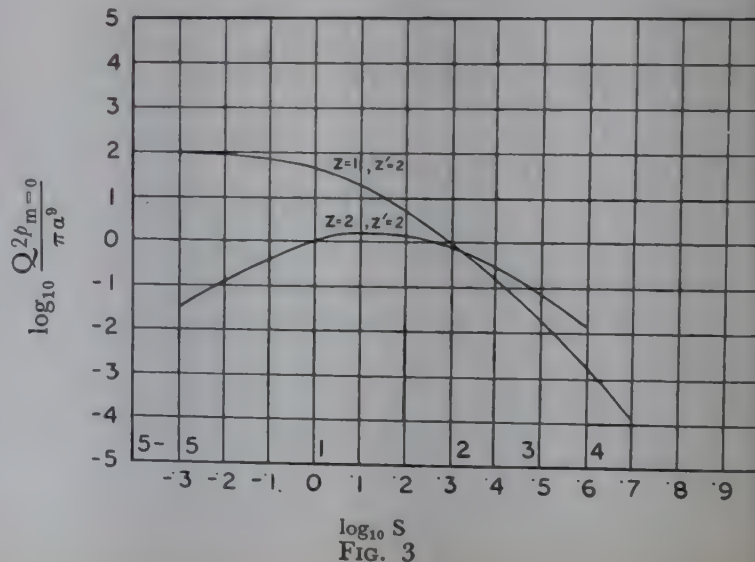


FIG. 3

The general method to work out this type of integrals has been given in appendix 3. We have finally

$$\left. \begin{aligned} Q_{m=0} &= \frac{2^9}{7} \cdot \frac{\pi^3 (2\pi\beta/V)^2}{a_s^5 a_{He}^5} \cdot \frac{e^4}{h^2 V^2} \left[\frac{1}{4a_{He}^2} + 4\pi^2 \frac{\beta^2}{V^2} \right]^{-7} \\ Q_{m=1} &= \frac{2^7}{3 \cdot 7} \cdot \frac{\pi^3}{a_s^5 a_{He}^5} \cdot \frac{e^4}{h^2 V^2} \left[\frac{1}{4a_{He}^2} + 4\pi^2 \frac{\beta^2}{V^2} \right]^{-6} \end{aligned} \right\} (38)$$

Reducing still further, we have finally

$$Q_{m=0} = \frac{2^{19}}{7} \cdot \frac{\pi a^2 \cdot z^5 z'^5 \cdot s^{10} \cdot [s^2 + z^2 - (z'^2/4)]^2}{[\{s^2 + (z+z'/2)^2\} \{s^2 + (z-z'/2)^2\}]^7}, \quad (39)$$

$$Q_{m=1} = \frac{2^{17}}{3 \cdot 7} \cdot \frac{\pi a^2 \cdot z^5 z'^5 \cdot s^{10}}{[\{s^2 + (z+z'/2)^2\} \{s^2 + (z-z'/2)^2\}]^6}. \quad (40)$$

DISCUSSION

Let us first compare the relative values of the different cross-section. We have for $z'=2$ and $z=1$.

$$\frac{Q_{2p_{m=\pm 1}}}{Q_{2p_{m=0}}} = \frac{s^2 + 2^2}{6s^2} \approx \frac{1}{6} \text{ when } s \text{ is large,}$$

$$\approx \frac{2}{3s^2} \text{ when } s \text{ is small.}$$

This shows that the probability of capture is much larger from $1s$ to $(2p)_{m=0}$ than from $1s$ to $(2p)_{m=\pm 1}$, except when $s < 1$.

Let us next compare $Q_{2p_{m=0}}$ to Q_{1s} . We have from (39) and (40)

$$\frac{Q_{2p_{m=0}}}{Q_{1s}} = \frac{10}{7} \frac{(s^2+9)^5 (s^2+1)^5}{s^8 (s^2+4)^7} \text{ for the case } z'=2 \text{ and } z=1.$$

$$\frac{Q_{2p_{m=0}}}{Q_{1s}} = 58.53 \quad 21.09 \quad 9.77 \quad 5.23 \quad 3.09 \quad 1.30 \quad 0.66 \quad 0.24$$

For $1s=1.0 \quad 1.25 \quad 1.5 \quad 1.75 \quad 2.0 \quad 2.5 \quad 3.0 \quad 4.0$

We thus obtain that for $z=1$ and $z'=2$, the capture cross-section $Q_{2p_{m=0}}$, though small compared to Q_{1s} , when $s \geq 4$, is no longer so when s continues to fall.

At $V=2$, i.e., when the α -particle has twice the velocity which the captured electron would have in its orbit, the ratio is nearly three times and at lower velocities it assumes a far higher value. Though there is some doubt whether these calculations can apply, when s becomes small, it appears that the probability of capture in excited states increases rapidly with diminishing s , i.e., towards the end of its path the charged particle would mostly be capturing the electron in the higher orbits. This is quite contrary to the view of Brinkman and Kramers that the capture probability in the higher orbits is negligible compared to that in the $1s$ -orbit.

We have not yet been able to finish our calculation for capture in ns or higher nd or nf orbits. These will be taken up in a later paper.

APPENDIX 1

To prove

$$\frac{1}{a_z^2} + 4\pi^2 \left\{ \frac{\beta}{V} - \sigma \right\}^2 = \frac{1}{a_{He}^2} + 4\pi^2 \frac{\beta^2}{V^2}$$

we have

$$\beta = v - v_0 + \frac{mV^2}{2h}$$

where

$$v = -\frac{h}{8\pi^2 m a_{He}^2}$$

$$v_0 = -\frac{h}{8\pi^2 m a_z^2}$$

On substitution $\frac{\beta}{V} = \frac{1}{8\pi^2 \sigma} \left(\frac{1}{a_z^2} - \frac{1}{a_{He}^2} \right) + \frac{\sigma}{2}$

where as usual $\sigma = \frac{mV}{h}$

or $\frac{1}{a_z^2} - \frac{1}{a_{He}^2} = \left(\frac{\beta}{V} - \frac{\sigma}{2} \right) 8\pi^2 \sigma = 4\pi^2 \left\{ \frac{\beta^2}{V^2} - \left(\frac{\beta}{V} - \sigma \right)^2 \right\}.$

Hence follows the result.

APPENDIX 2

The integral $I_1 = \int_0^\pi e^{iB \cos \theta} J_0(k \sin \theta) \sin \theta d\theta.$

We have on putting the standard form of J_0 ,

$$\begin{aligned} I_1 &= \Sigma \frac{(-1)^m \left(\frac{1}{2}k\right)^{2m}}{(m!)^2} \int_0^\pi e^{iB \cos \theta} (\sin \theta)^{2m+1} d\theta \\ &= \frac{(-1)^m \left(\frac{1}{2}k\right)^{2m}}{(m!)^2} \frac{\Gamma(m+\frac{1}{2})}{\left(\frac{1}{2}B\right)^{m+\frac{1}{2}}} \Gamma\left(\frac{1}{2}\right) J_{m+\frac{1}{2}}(B) \\ &= \Sigma \frac{\Gamma\left(\frac{1}{2}\right) \sqrt{2}}{m!} k^{2m} \left(\frac{d}{2BdB}\right)^m \left\{ B^{-\frac{1}{2}} J_{\frac{1}{2}}(B) \right\} \\ &= 2\Sigma \frac{1}{m!} \left(k^2 \frac{d}{2BdB}\right)^m \left\{ \frac{\sin B}{B} \right\} \\ &= 2 \frac{\sin \sqrt{B^2+k^2}}{\sqrt{B^2+k^2}}. \end{aligned}$$

The integral $I_3 = \int_0^\pi e^{iB \cos \theta} J_1(k \sin \theta) \sin^2 \theta d\theta.$

Let us take the integral

$$I_2 = \int_0^\pi e^{iB \cos \theta} J_0(k \sin \theta) \sin \theta \cos \theta d\theta$$

and integrate the above by parts: we have

$$I_2 = \frac{1}{k} \left[e^{iB \cos \theta} \sin \theta J_1(k \sin \theta) \right]_0^\pi + \frac{iB}{k} \int_0^\pi e^{iB \cos \theta} J_0(k \sin \theta) \sin^2 \theta d\theta.$$

The first term vanishes and it can be easily shown that

$$I_2 = -\frac{1}{i} \frac{dI_1}{dB},$$

so we have

$$I_3 = -\frac{k}{B} \frac{dI_1}{dB} = \frac{2k}{B^2 + k^2} \left\{ \frac{\sin \sqrt{B^2 + k^2}}{\sqrt{B^2 + k^2}} - \cos \sqrt{B^2 + k^2} \right\}$$

APPENDIX 3

The evaluation of the integrals of the general type $\int_0^\infty x^m \{K_\nu(x)\}^2 dx$ is due to Dr. F. C. Auluck of the Delhi University to whom we express our thanks.

$$I_m = \int_0^\infty x^m dx \{K_\nu(x)\}^2 = \int_0^\infty x^m du \int_0^\infty \int_0^\infty e^{-x(\cosh t + \cosh t')} \cos vt \cos vt' dt dt'.$$

Further the integral on the right hand side is the coefficient of $(-1)^m (a^m/m!)$ in the integral

$$I = \int_0^\infty \int_0^\infty \int_0^\infty e^{-x(a + \cosh t + \cosh t')} \cos vt \cos vt' dt dt' dx = \int_0^\infty \int_0^\infty \frac{\cos vt \cos vt'}{a + \cosh t + \cosh t'} dt dt' \quad (\text{on integration with respect to } x) = \frac{1}{2} \int_0^\infty \int_0^\infty \frac{\cosh v(t+t') + \cosh v(t-t')}{a + 2 \cosh (t+t')/2 \cdot \cosh (t-t')/2} dt dt'.$$

If we put

$$t+t' = 2x$$

$$t-t' = 2y$$

we get

$$I = \int \int \frac{\cosh 2vx + \cosh 2vy}{a + 2 \cosh x \cosh y} dx dy = \int_{x=0}^\infty \int_{y=0}^\infty \frac{\cosh 2vx}{a + 2 \cosh x \cosh y} dx dy$$

$$+ 2 \int_{y=0}^\infty \int_{x=0}^\infty \frac{\cosh 2vy}{a + 2 \cosh x \cosh y} dx dy$$

$$= 2 \int_{x=0}^\infty \int_{y=0}^\infty \frac{\cosh 2vx}{a + 2 \cosh x \cosh y} dx dy$$

$$= 2 \int_{x=0}^\infty \frac{\cosh 2vx}{\sqrt{4 \cosh^2 x - a^2}} \cos^{-1} \frac{2 \cosh x + a \cosh y}{a + 2 \cosh x \cosh y} dx \Bigg]_{y=0}^\infty$$

assuming $a < 2$.

$$= \int_0^\infty \frac{\cosh 2vx}{\sqrt{4 \cosh^2 x - a^2}} \cos^{-1} \frac{a}{2 \cosh x} dx.$$

Expanding $\frac{1}{\sqrt{4 \cosh^2 x - a^2}}$ and $\cos^{-1} \frac{a}{2 \cosh x}$ in series

$$I = \int_0^\infty \frac{\cosh 2vx}{\cosh x} \left[\frac{\pi}{2} - \frac{a}{2 \cosh x} + \frac{\pi}{2} \frac{1}{2!} \frac{a^2}{(2 \cosh x)^2} - \frac{2^3}{3!} \frac{a^3}{(2 \cosh x)^3} + \frac{\pi}{2} \frac{1^2 \cdot 3^2}{4!} \frac{a^4}{(2 \cosh x)^4} - \frac{2^2 \cdot 4^2}{5!} \frac{a^5}{(2 \cosh x)^5} + \frac{\pi}{2} \frac{1^2 \cdot 3^2 \cdot 5^2}{6!} \frac{a^6}{(2 \cosh x)^6} - \frac{2^2 \cdot 4^2 \cdot 6^2}{7!} \frac{a^7}{(2 \cosh x)^7} \dots \right] dx.$$

Hence for $m \geq 4$

$$I_m = \int_0^\infty x^m dx \int \int e^{-x(\cosh t + \cosh t')} \cosh vt \cosh vt' dt dt' = \frac{2^2 \cdot 4^2 \cdot 6^2 \dots (m-1)^2}{2^m} \int_0^\infty \frac{\cosh 2vx}{\cosh^{m+1} x} dx, \text{ if } m \text{ is odd.} = \frac{\pi}{2} \frac{1^2 \cdot 3^2 \cdot 5^2 \dots (m-1)^2}{2^m} \int_0^\infty \frac{\cosh 2vx}{\cosh^{m+1} x} dx, \text{ if } m \text{ is even.}$$

The cases that concern us are for $\nu=2$ and $\nu=3$. For $\nu=2$, the expression under the integral may be written as

$$\int_0^\infty \frac{\cosh 4x}{\cosh^{m+1} x} = \frac{(m+1)(m+3)}{m(m-2)} \int_0^\infty \text{sech}^{m-3} x dx$$

From which follows

$${}^2I_4 = \frac{315}{256} \pi^2,$$

$${}^2I_5 = \frac{2^5}{5}$$

$${}^2I_6 = \frac{3^3 \cdot 175}{2^{11}} \pi^2,$$

$${}^2I_7 = \frac{3 \cdot 2^6}{7}$$

Similarly for $\nu=3$

$${}^3I_7 = \frac{2^7 \cdot 3}{7}$$

ACKNOWLEDGEMENTS

One of us (D. Basu) has been receiving a scholarship from the Radio Research Committee of the Council of Scientific and Industrial Research, Government of India, and wishes to express his grateful thanks for the financial assistance.

PALIT LABORATORY (PHYSICS),
CALCUTTA UNIVERSITY.

REFERENCES

- BRINKMAN, H. C. and KRAMERS, 1930, *Proc. Amst.*, **33**, 973.
 FOWLER, R. H., 1924, *Phil. Mag.*, **47**, 257.
 HENDERSON, G. H., 1923, *Proc. Roy. Soc.*, **102**, 496.
 HYLLEBERG, E. A., 1937, *Zs. f. Phys.*, **106**, 305.
 JACOBSEN, J. C., 1930, *Phil. Mag.*, **10**, 401.
 OPPENHEIMER, J. R., 1928, *Phys. Rev.*, **31**, 349.
 PANNEKOCK and MINNAERT, 1928, *Proc. Amst.*, **31**, 104.
 PEREPELKIN, E. J., and MELNIKOV, O. A., 1935, *Pulkovo Bulletin*, **14**, 1.
 RUTHERFORD, E., 1924, *Phil. Mag.*, **47**, 277.
 SAHA, M. N., 1942, *Proc. Nat. Inst. Sc.*, **8**, 99.
 THOMAS, L. H., 1927, *Proc. Roy. Soc.*, **114**, 561.

75. WAVE TREATMENT OF PROPAGATION OF ELECTRO-MAGNETIC WAVES IN THE IONOSPHERE

M. N. SAHA* AND B. K. BANERJEA

(*Ind. Jour. Phys.*, **19**, 159, 1945.)

ABSTRACT

Wave-equations for the propagation of e m. waves through the ionosphere have been obtained by the use of a new mathematical method involving the use of dyadic analysis introduced by Gibbs. Expressions for steady current conductivity of the ionosphere have been obtained by this method and the results are concordant with those of Chapman; an extra term for the conductivity, which is more prominent in the F_2 -layer has been obtained.

It has been shown that the wave is split up into three waves, as in Zeeman effect, one of which is ordinary, the other two extraordinary, in accordance with observations by Toshniwal, and Harang.

1. INTRODUCTION

The subject of propagation of electromagnetic waves in the ionosphere appears to be at the present time in a rather confused state. Appleton (1932), in his pioneering work, used what is now commonly known the ray treatment, i.e., starting from Maxwell's equations, he obtained a value of the refractive index of the e.m. waves in terms of the electron concentration, the earth's magnetic field and the damping coefficient of electrons. He further postulated that the wave gets reflected when the refractive index vanishes. From the two values of refractive index it was deduced that the wave splits up into two, one ordinary and the other extraordinary and the sense of polarisation of each wave was determined. The condition of reflection of the extraordinary wave is, however, satisfied, at two distinct levels given by the condition $p_0^2 = p^2 \pm pp_h$. It appears to have been assumed that only one of these waves, corresponding to the negative sign existed. Toshniwal (1935) and Harang (1936) have however, obtained at times reflections corresponding to the conditions $p_0^2 = p^2 +$

pp_h , so that it is legitimate to think that the wave really gets split into three components on entry into the ionosphere, one of which fails usually to get reflected owing to heavy absorption. Further, we have to explain the phenomena of M-reflections, which prove that the wave does not get completely reflected even when $\mu=0$, but may leak through the ion-layer in considerable intensity, and get reflected from a higher layer.

The wave treatment was first attempted by Hartree (1929, 1931) in three important papers. The papers of Hartree are extremely difficult to follow on account of the difficult notations used and some unnecessary complications introduced. He used throughout the notation of dyadics, introduced by Gibbs. This notation, though much convenient for mathematical working is not generally familiar and to make the deductions intelligible the results have to be transcribed to ordinary notations which was not carried out by Hartree. Hartree obtained the displacement of the electron or the ion as $\mathbf{S} \cdot \mathbf{E}$ where $\mathbf{S}$ is a tensor, $\mathbf{E}$ =Electric field. This part is rendered rather complicated because the electron is regarded as bound by a quasi-elastic force. From the expression for $\mathbf{S}$, he obtained an expression for σ called the scattering tensor. The underlying

*Fellow of the Indian Physical Society.

physical idea is borrowed from a paper by Darwin (1925), who has shown that almost all optical phenomena, e.g. reflection and refraction can be explained in terms of scattering by elementary constituents of the medium. Hartree has shown from the equivalence of two different processes that the equation of propagation of the electromagnetic waves in the ionosphere continues to obey the Maxwellian form. The treatment was also rendered complicated by the introduction of the term β , the Lorentz polarisation term which he took not much far from $1/3$. It has, however, been shown by Darwin (1934) that $\beta=0$, and this considerably simplifies Hartree's method. The expression for refractive index was obtained by considering the case of normal incidence in a stratified medium where μ is supposed to be constant. He ultimately obtains the same result as Appleton. So far his treatment led to a justification rather than laying the foundations of a rigorous wave treatment. In a later paper he takes the wave equation with a variable μ and tries to solve this equation for a few simple cases but it is obvious none of these assumptions corresponds to reality.

Saha, Rai and Mathur (1937) expressed the displacement of the ions in simpler analytical form, which may be shown identical with those of Hartree in spite of the apparent differences in form. From this displacement they obtained the value of the dielectric tensor for a stratified medium and ultimately obtained the same expression for μ as that of Appleton. The wave treatment was applied in a simple case for the O-wave and the penetrability of the electron barrier for a simple case was deduced.

In the present paper the foundations of a rigorous wave treatment have been laid down and the expressions for refractive index, conductivity and direct current conductivity have been deduced. The solution of the wave-equations has not yet been tried.

2. THE DISPLACEMENT OF THE IONS IN THE IONOSPHERE

The equation of motion of the charged ions referred to any system of axes can be written in the form

$$\frac{d^2 \mathbf{r}}{dt^2} + \nu \frac{d\mathbf{r}}{dt} + \frac{e}{m_0 c} [\mathbf{H} \times \frac{d\mathbf{r}}{dt}] = \frac{e\mathbf{E}}{m_0}, \quad \dots (1)$$

where $\mathbf{r}$ =displacement vector of the ions with components (ξ, η, ζ) ,

m_0 =mass of the ions,

ν =collision frequency of the ions,

$\mathbf{H}$ =Earth's magnetic field with direction cosines l, m, n ,

$\mathbf{E}=\mathbf{E}_0 \cos pt$, the electric vector of the incident e.m. wave with direction cosines l', m', n' .

The effect of the magnetic vector and space charge have been omitted as usual. The notation conforms as closely as

possible to those used by Appleton (1932) and Saha, Rai and Mathur (1937).

It can be easily verified that the solution of the above equation with $\mathbf{E}=\mathbf{E}_0 \cos pt$ is the real part of the solution when we put $\mathbf{E}=\mathbf{E}_0 e^{ipt}$; we use $\mathbf{E}$ in this form, because the solution is now easy to obtain. The quantity analogous to static conductivity now comes out to be complex (Stratton 1939) whose real part gives ordinary conductivity, imaginary part gives the deviation of the refractive index from unity.

Starting with $\mathbf{E}=\mathbf{E}_0 e^{ipt}$ and introducing the notations

$$p_0^2 = \frac{4\pi N e^2}{m_0}; \quad \alpha = i\nu p - p^2; \quad p_h = \frac{eH}{m_0 c};$$

$$\beta = ip p_h; \quad \mathbf{r} = (\xi, \eta, \zeta) e^{ipt}.$$

and breaking up the above equation into components we get

$$\begin{aligned} \alpha \xi + ip p_h (m \zeta - n \eta) &= \frac{e}{m_0} l' E_0 \\ \alpha \eta + ip p_h (n \xi - l \zeta) &= \frac{e}{m_0} m' E_0 \quad \dots (2) \\ \alpha \zeta + ip p_h (l \eta - m \xi) &= \frac{e}{m_0} n' E_0. \end{aligned}$$

Solving these equations by the usual determinant method, we have

$$\left. \begin{aligned} \xi &= \frac{e E_0}{m_0} \left[\frac{l'(\alpha^2 + \beta^2 l^2) + m'(\alpha \beta n + \beta^2 m l)}{\alpha(\alpha^2 + \beta^2)} + n'(\beta^2 n l - \beta \alpha m) \right] \\ \eta &= \frac{e E_0}{m_0} \left[\frac{l'(\beta^2 m l - \beta \alpha n) + m'(\alpha^2 + \beta^2 m^2)}{\alpha(\alpha^2 + \beta^2)} + n'(\beta^2 m n + \beta \alpha l) \right] \\ \zeta &= \frac{e E_0}{m_0} \left[\frac{l'(\beta^2 n l + \beta \alpha m) + m'(\beta^2 m n - \beta \alpha l)}{\alpha(\alpha^2 + \beta^2)} + n'(\alpha^2 + \beta^2 n^2) \right] \end{aligned} \right\} \dots (3)$$

Let σ denote the complex conductivity. We have

$$\sigma \cdot \mathbf{E} = \text{current} = -N e \frac{d\mathbf{r}}{dt} = -ip N e \mathbf{r}. \quad \dots (4)$$

Substituting the value of $\mathbf{r}$ from (3), we get σ in the tensor form

$$\sigma = \frac{-m_0 / ip N e^2}{\alpha(\alpha^2 + \beta^2)} \begin{vmatrix} \alpha^2 + \beta^2 l^2 & \beta^2 m l - \beta \alpha n & \beta^2 n l + \beta \alpha m \\ \beta^2 l m + \beta \alpha n & \alpha^2 + \beta^2 m^2 & \beta^2 m n - \beta \alpha l \\ \beta^2 n l - \beta \alpha m & \beta^2 m n + \beta \alpha l & \alpha^2 + \beta^2 n^2 \end{vmatrix} \quad (5)$$

Let us next find out the principal axes of the tensor ellipsoid by using the Hamilton-Cayley method. The principal components are given by the roots of the equation,

$$\lambda^3 - \Phi_1 \lambda^2 + \Phi_2 \lambda - \Phi_3 = 0, \quad \dots (6)$$

where Φ_1 =spur of the tensor, $\sigma, q=x, y, z$

$$\Phi_2 = \Sigma (\sigma_{qq} \sigma_{ss} - \sigma_{qs} \sigma_{sq}) \quad s, q = x, y, z, \quad s \neq q$$

$$\Phi_3 = \text{Determinant of } \sigma.$$

We obtain from (5)

$$\Phi_1 = 3\alpha^2 + \beta^2; \Phi_2 = 3\alpha^2(\alpha^2 + \beta^2); \Phi_3 = \alpha^2(\alpha^2 + \beta^2)^2$$

Hence the cubic equation reduces to

$$\lambda^3 - (3\alpha^2 + \beta^2)\lambda^2 + 3\alpha^2(\alpha^2 + \beta^2)\lambda - \alpha^2(\alpha^2 + \beta^2)^2 = 0$$

$$\text{or } [\lambda - (\alpha^2 + \beta^2)] [\lambda - (\alpha^2 + i\alpha\beta)] [\lambda - (\alpha^2 - i\alpha\beta)] = 0. \quad (7)$$

If $\nu=0$, α , $i\alpha\beta$, and β^2 are all real, and the roots are all real, such a dyad has been classified by Gibbs as a tonic dyad.

In general case, for $\nu \neq 0$, we separate the complex conductivity tensor σ in (5) into real, and imaginary parts. Then forming the corresponding Hamilton-Cayley equations for the real and the imaginary parts we get the roots for $\text{Re}\sigma$ as

$$\lambda_1 = \frac{Ne^2}{m\rho} \cdot \frac{\nu}{p^2 + \nu^2}; \lambda_2 = \frac{Ne^2}{m\rho} \cdot \frac{\nu + ip_h}{p^2 + (\nu + ip_h)^2};$$

$$\lambda_3 = \frac{Ne^2}{m\rho} \cdot \frac{\nu - ip_h}{p^2 + (\nu - ip_h)^2} \quad (8)$$

and for $\text{Im}\sigma$

$$\lambda_1 = \frac{Ne^2}{m} \cdot \frac{1}{p^2 + \nu^2}; \lambda_2 = \frac{Ne^2}{m} \cdot \frac{1}{p^2 + (\nu + ip_h)^2};$$

$$\lambda_3 = \frac{Ne^2}{m} \cdot \frac{1}{p^2 + (\nu - ip_h)^2} \quad (9)$$

Dyads of this type, having two complex conjugate roots of the H. C. equation are classified by Gibbs as cyclotonic dyad. All the properties of the ionosphere are of this type.

Let us next find out the orientation of the characteristic principal axis of the tensor σ , to the earth's magnetic field.

We consider a vector ρ such that

$$\sigma\rho = \lambda\rho$$

where λ is a proportionality factor. If I_0 be the idem factor

$$\sigma\rho = \lambda I_0\rho \quad \text{or} \quad (\sigma - \lambda I_0)\rho = 0$$

$$\text{i.e.} \quad \left. \begin{aligned} (\sigma_{11} - \lambda_1)L + \sigma_{12}M + \sigma_{13}N &= 0 \\ \sigma_{21}L + (\sigma_{22} - \lambda_1)M + \sigma_{23}N &= 0 \\ \sigma_{31}L + \sigma_{32}M + (\sigma_{33} - \lambda)N &= 0 \end{aligned} \right\} \quad \dots \quad (10)$$

where L , M , N are the direction cosines of the principal axis. Substituting $\lambda = \alpha^2 + \beta^2$ and the corresponding values of σ_{11} , σ_{12} , etc., and remembering that $L^2 + M^2 + N^2 = 1$

$$\text{we get } L = \pm l, M = \pm m, N = \pm n. \quad \dots \quad (11)$$

We thus see that the real characteristic principal axis of the tensor σ coincides with the earth's magnetic field. Similarly we can show that the other properties like ordinary conductivity, dielectric constant, etc., have the same characteristic principal axis. The other two axes of the cyclotonic dyad are in a plane perpendicular to this axis, and may be oriented arbitrarily.

Let us next choose a new system of axes with the direction of the earth's magnetic field as the X-axis, Z-axis being in the magnetic meridian and Y axis horizontal perpendicular to the magnetic meridian. Referred to this new coordinate system, let us now express the displacements and the tensor σ in the new coordinates, We put $l=1$, $m=n=0$ in (5). Then

$$\sigma = \frac{-ipNe^2/m_0}{\alpha(\alpha^2 + \beta^2)} \begin{vmatrix} \alpha^2 + \beta^2 & 0 & 0 \\ 0 & \alpha^2 & -\alpha\beta \\ 0 & \alpha\beta & \alpha^2 \end{vmatrix} \quad \dots \quad (12)$$

and from (3)

$$\xi = \frac{eE}{m_0} [l'(\alpha^2 + \beta^2)] / [\alpha(\alpha^2 + \beta^2)]$$

$$\eta = \frac{eE}{m_0} [\alpha^2 m' + \beta \alpha n'] / [\alpha(\alpha^2 + \beta^2)] \quad \dots \quad (13)$$

$$\zeta = \frac{eE}{m_0} [\alpha^2 n' - \beta \alpha m'] / [\alpha(\alpha^2 + \beta^2)].$$

Let us next form that the real parts of the displacements, which are the true solutions of equation (1) with $E = E_0 \cos pt$. We have, putting $E(l', m', n') = (E_x, E_y, E_z)$

$$\text{Re } \xi = - \frac{eE_x}{m_0(p^2 + \nu^2)} \left[\cos pt - \frac{\nu}{p} \sin pt \right] \quad \dots \quad (14)$$

$$(\text{Re } \eta \pm i \text{Re } \zeta) = - \frac{e(E_y \pm iE_z)}{m_0[p^2 + (\nu \pm ip_h)^2]} \left\{ \cos pt - \frac{\nu \pm ip_h}{p} \sin pt \right\}$$

From the above expressions, we can easily obtain expressions for the steady current electrical conductivity in the ionosphere as obtained by Schuster, Chapman and Pedersen. We have to put $p=0$

We get

$$\xi = - \frac{eE_x}{m_0}; \quad \eta = \frac{e}{m_0(p_h^2 + \nu^2)} [\nu E_y + p_h E_z];$$

$$\zeta = \frac{e}{m_0(p_h^2 + \nu^2)} [\nu E_z - p_h E_y]$$

We have therefore

$$I_x = Nc\xi = \frac{Ne^2}{mv} E_x \quad \text{and}$$

$$\sigma_x = I_x/E_x = \text{conductivity parallel to the magnetic field}$$

$$= \frac{Ne^2}{mv}. \quad \dots \quad (15)$$

If now $E_z=0$, i.e. the e.m.f. is in the horizontal plane perpendicular to the magnetic meridian, we have

$$\sigma_y = \frac{Ne^2}{m_0} \cdot \frac{\nu}{(\nu^2 + p_h^2)}. \quad \dots \quad (16)$$

This is known as the transverse conductivity.

We have an additional current along the Z -axis, i.e., in the meridian plane perpendicular to the lines of force, and the conductivity

$$\sigma_z = -\frac{Ne^2\rho_z}{m_0v^2 + \rho_z^2} \quad \dots (17)$$

If $E_z \neq 0$, but $E_y = E_x = 0$, we have flow of currents both along Y and Z axes.

We observe from these results that even when v tends to zero as in the F region, we have a conductivity transverse to the magnetic meridian $= \frac{Ne^2}{m_0} \cdot \frac{\rho_z}{(v^2 + \rho_z^2)}$ and this has a limiting value $\frac{Ne^2}{m_0\rho_z}$.

We have thus got an extra term for transverse conductivity, viz. $\frac{Ne^2}{m_0} \cdot \frac{\rho_z}{(v^2 + \rho_z^2)}$ in addition to those already known but we have not yet had time to examine its probable contribution to the theory of L and S terms in geomagnetism.

3. THE FUNDAMENTAL MAXWELLIAN EQUATIONS

The fundamental equations for the propagation of the e.m. waves in the ionosphere are

$$\nabla \times \mathbf{H} = \frac{1}{c} \dot{\mathbf{E}} + \frac{4\pi}{c} \mathbf{I} \quad \dots (18)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \dot{\mathbf{H}}$$

$$\nabla \cdot \mathbf{E} = 4\pi \rho$$

$$\nabla \cdot \mathbf{H} = 0$$

Here ' $\mathbf{I}$ ' denotes total current, which requires some elucidation. We have $\mathbf{I} = \sigma \cdot \mathbf{E}$, where $\mathbf{E}$ = total field (i.e. sum of incident field plus radiation field due to surrounding ions.) Also in the ionosphere, it is customary to take $\rho = 0$. Thus (18.1) is modified as

$$\nabla \times \mathbf{H} = \frac{1}{c} \dot{\mathbf{E}} - \frac{4\pi\sigma \cdot \mathbf{E}}{c}$$

It can now be easily shown, taking curl of curl $\mathbf{E}$, etc., that $\mathbf{E}$ satisfies the equation

$$\nabla^2 \mathbf{E} - \frac{\ddot{\mathbf{E}}}{c^2} = -\frac{4\pi}{c^2} \cdot \sigma \dot{\mathbf{E}}$$

$$\text{or} \quad \nabla^2 \mathbf{E} + \frac{k^2}{c^2} \left(1_0 + \frac{4\pi i \sigma}{\rho} \right) \cdot \mathbf{E} = 0 \quad \dots (19)$$

and similarly $\mathbf{H}$ satisfied the equation

$$\nabla^2 \mathbf{H} - \frac{1}{c^2} \ddot{\mathbf{H}} = -\frac{4\pi}{c} \nabla \times (\sigma \cdot \mathbf{E}) \quad \dots (20)$$

Now for σ we have to substitute in the case of any coordinate system expressions (5), but it will simplify matters if we introduce the principal coordinates defined in (12). We have then

$$1_0 = \frac{1-\sigma}{\rho} = \begin{vmatrix} 1 + \frac{\rho_0^2}{\alpha^2} & 0 & 0 \\ 0 & 1 + \frac{\rho_0^2 \alpha}{\alpha^2 + \beta^2} & -\frac{\rho_0 \beta}{\alpha^2 + \beta^2} \\ 0 & +\frac{\rho_0 \beta}{\alpha^2 + \beta^2} & 1 + \frac{\rho_0^2 \beta}{\alpha^2 + \beta^2} \end{vmatrix} \quad (21)$$

The equations (19) can then be split up into three equations

$$\nabla^2 E_x + \frac{k^2}{c^2} \left(1 - \frac{\rho_0^2}{\rho^2 + \rho_0^2} \right) E_x = 0, \quad \dots (22)$$

$$\nabla^2 E_y + \frac{k^2}{c^2} (b E_y - c E_z) = 0,$$

$$\nabla^2 E_z + \frac{k^2}{c^2} (\rho E_y + b E_z) = 0,$$

$$\text{where} \quad b = 1 + \frac{\rho_0^2 \alpha}{\alpha^2 + \beta^2}, \quad c = \frac{\rho_0 \beta}{\alpha^2 + \beta^2}.$$

The last two equations had better be written in the form

$$\nabla^2 (E_y + i E_z) + \frac{k^2}{c^2} \left\{ 1 - \frac{\rho_0^2}{\rho^2 + \rho_0^2 + i \rho \rho_0} \right\} (E_y + i E_z) = 0. \quad (23)$$

From these equations, we see clearly that on entrance into the ionosphere, the three components E_x , $E_y + i E_z$, $E_y - i E_z$, travel with different velocities, depending on ρ_0^2 , v , and ρ_z . If these quantities are slowly varying, we can talk of refractive index. The E_x -component (electric displacement parallel to the magnetic field) has the complex refractive index

$$\mu_0 = 1 - \frac{\rho_0^2}{\rho^2 - i \rho v}$$

and the $E_y + i E_z$, $E_y - i E_z$ components have the refractive indices

$$\mu_\pm = 1 - \frac{\rho_0^2}{\rho^2 - i \rho v \mp \rho \rho_z}$$

The analogy with Zeeman-effect is obvious; $(E_y + i E_z)$ denote anticlock-wise circular polarisation and $(E_y - i E_z)$ denote clockwise circular polarisation. If we neglect v and put $\mu_0 = 0$ we get Appleton's conditions for the reflexion of the σ -wave, $\rho_0^2 = \rho^2$, and if we put $\mu_\pm = 0$, we get the two conditions for the reflexion of the two extraordinary waves $\rho_0^2 = \rho^2 \mp \rho \rho_z$, which have different sense of polarisation.

The complete solution of the equations (21), however, is rather difficult, for we are using a coordinate system

which, except at the magnetic equator, and at the magnetic poles, cannot be linked to the local coordinates in a simple manner.

At the magnetic equator the X and Y axis are horizontal and Z-axis is vertical. In a vertical propagation of the e.m. waves $E_x = 0$, and we have only E_y and E_z components. The reflected wave will therefore have its o -component polarized parallel to the magnetic field, the x -component polarized parallel to the Y-axis, i.e., perpendicular to the magnetic field in a horizontal direction. We have, however, not yet tried to evaluate E_o , E_x in terms of the amplitudes of the wave sent out by the antenna.

For the magnetic pole, the X-axis is vertical, and for a vertical propagation we have $E_z = 0$, and we have only E_x and E_y , i.e., two circularly polarized X-waves. We have not obtained the reflexion coefficient from a solution of (21), which will be attempted in a future paper.

One of us, B. K. Banerjee, has been the recipient of a Research Scholarship from the Indian Research Committee of the Council of Scientific and Industrial Research, and wishes to express his thanks to the Council for facility to work, and permission to publish this paper.

REFERENCES

- APPLETON, 1932, *Journ. Inst. Elec. Eng.*, **71**, 646.
 CHAPMAN and BARTELL, 1940, *Geomagnetism*, Vol. 1, p. 524.
 DARWIN, 1925, *Trans. Camb. Phil. Soc.*, **23**, 1940.
 DARWIN, 1934, *P. R. S.*, **146**, 17.
 GIBBS and WILSON, 1907, *Vector Analysis*.
 HARANG, 1936, *Terrestrial Magnetism*, **41**, 143.
 HARTREE, 1929, *Proc. Camb. Phil. Soc.*, **25**, 97.
 HARTREE, 1931, *Proc. Camb. Phil. Soc.*, **27**, 143.
 SAHA, RAI and MATHEW, 1937, *Proc. Nat. Inst.*, **4**, 53.
 STRATTON, 1942, *Electromagnetic Theory*, p. 326.
 TOMBIWAL, 1935, *Nature*, **135**, 471.

76. A PHYSICAL THEORY OF THE SOLAR CORONA*

(*Proc. Phys. Soc. Lond.*, **57**, 271, 1945.)

Lecture delivered 23 November 1944; MS. received 6 April 1945.

§ 1. INTRODUCTION

Nearly twenty-five years ago, when the present writer was preparing his paper "On a physical theory of stellar spectra" (Saha, 1921), he had the benefit of very sound advice from the late Professor Alfred Fowler, who allowed him to make free use of his (Fowler's) own unrivalled knowledge of spectroscopy and of stellar spectra. Fowler's remarks on this theory, which to my knowledge were never put in print, may now be disclosed. "The thermal ionization theory", he told me repeatedly, "accounts in a general way for the spectra of normal stars; but there are very important exceptions, e.g. the stars with peculiar spectra, the planetary nebulae; even in the case of normal stars, the great strength of Balmer lines of hydrogen which persists throughout all stellar classes is a disquieting feature, and in the case of the sun, the peculiar behaviour of helium cannot, in my opinion, be accounted for by the thermal ionization theory at all".

During the past twenty-five years, many of these points raised by Fowler have been taken up by well-known workers: Darwin, R. H. Fowler and Milne, Zanstra, and others in this country, mostly on the theoretical side; and

by Russell, Bowen, Struve, Menzel, Payne, and their co-workers in the U.S.A., Unsöld, Pannekoek, and other workers on the Continent. But the helium problem appears to have remained very much as it was twenty-five years ago. Briefly the problem is as follows: The Fraunhofer spectrum of the sun shows only the lines of such elements as have excitation potentials (energy values of the lower state) between zero and 10 volts; in the chromospheric spectrum, the lines of ionized elements are relatively stronger but in no case, helium excepted, do we get lines of stronger excitation than 14 to 15 volts (energy value of upper state). The lines of He do not occur at all in the normal Fraunhofer spectrum, except over disturbed regions, like penumbra of sunspots, but occur prominently in the flash spectrum up to heights of 7500 km. These lines have an excitation potential exceeding 20 volts; but the line of ionized helium $\lambda 4686$, $\nu = 4R \left(\frac{1}{3^2} - \frac{1}{4^2} \right)$ occurs as a prominent but low-level chromospheric line scarcely exceeding 2000 km. in height. This line has an excitation potential of about 75 volts, and one fails to see how such high excitation can exist in the sun, and that too in the lower levels.

The points were repeatedly urged by Professor A. Fowler, and were repeated by myself later on many occasions and have also received attention from others.

*For fuller details, see Saha (1942).

There are certain additional features regarding the occurrence of He lines. I think it was Evershed who first drew attention to the fact that the chromospheric He lines tend to get fainter and ultimately disappear towards the limb. The matter was confirmed by Pannekoek, and Minnaert (1928), and more fully by Perepelkin and Melnikov (1935). The findings of the later workers are represented in table 1 and figure 1, taken from their works.

TABLE 1

Height (km.)	E (erg/cm. ² sec.)	Height (km.)	E (erg/cm. ² sec.)
500	39×10^{-6}	4000	60×10^{-6}
1000	125	4500	29
1500	186	5000	12
2000	212	5500	4.3
2500	195	6000	1.3
3000	151	6500	0.3
3500	100	7000	0.1

These results are inexplicable on the ionization theory, or any modification of it. For some time past I have been thinking of another explanation, which I hesitated to put forward on account of its radically heterodox nature. Allowing that He exists in some quantity in the solar atmosphere, it is clear that neither the ultra-violet radiation from the sun nor the thermal conditions existing on the

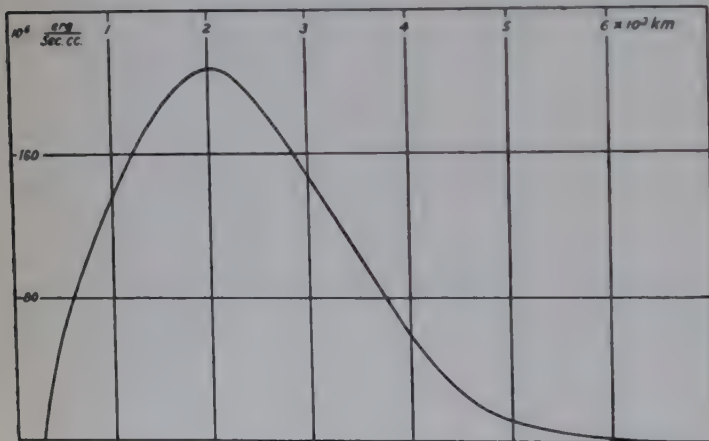


Fig. 1

surface of the photosphere is capable of exciting it to luminescence in the way we obtain in the sun. The suggestion regarding their origin is as follows:—First, suppose that α -particles are constantly being produced throughout the solar surface, as a result of some nuclear reaction, and hurled forth through the solar atmosphere. As they pass through the solar gases (mostly hydrogen), they go on ionizing these atoms by collision (as in J. J. Thomson's theory of ionization by collision), and continuously losing energy. When their energy has sufficiently

diminished, they capture an electron in any orbit and become normal or excited He^+ . The excited He^+ atom may radiate energy of which only $\lambda 4686$, and possibly the lines $\nu = 4R \left(\frac{1}{4^2} - \frac{1}{m^2} \right)$, are within observable range. The He^+ atom moves forward along the original direction but it goes on losing energy, which is spent, as in the case of He^{++} , in releasing electrons from atoms by collision. When its velocity of motion has sufficiently diminished, it may capture a second electron, and become a normal or excited He atom. The excited He atom gives us the high-level chromospheric He lines.

This phenomenon of capture of electrons by α -particles to form He^+ and He was discovered by Rutherford and Henderson (1923) while studying α -tracks in the cloud-chamber. The capture of the first electron begins to take place when the velocity of the α -particle has fallen to $2c\alpha$, where c is the velocity of light and α the Sommerfeld constant. It may be recalled that $c\alpha$ is the velocity of the electron moving in the first orbit of the H atom. We have $c\alpha = 2.18 \times 10^6 \text{ km./sec.}$ We shall have frequently to express velocities in this paper in terms of $c\alpha$ as unit in the form $V = sc\alpha$, where s is a numerical coefficient. In the cloud-chamber, when the α -particle starts to move, it does so with a velocity of the order of $9c\alpha$ (for α -particles of range 11 cm. from Th C²²). It goes on producing electrons by collision, and thus gradually loses energy. When the last centimetre is reached, and its velocity has reached $2c\alpha$, corresponding to an energy of 1×10^5 volts, and range of about 0.46 cm., the α -particle begins to capture electrons to an appreciable degree.

But He^+ which is formed by the capture of an electron may again lose this electron by collision with atoms, and again become He^{++} or α -particle. In fact Rutherford (1924) showed that this alternate loss and capture of electrons may occur thousands of times within the last millimetre of the range of the α -particle, but all the time the velocity of the α -particle or of He^+ is falling, and when it reaches $\simeq c\alpha$, He^+ may capture a second electron from cloud-chamber gases and become He. But this may be again ionized to He^+ , until ultimately we get He, and the track terminates.

A mathematical theory of this effect has been worked out by Oppenheimer (1928) and by Kramers and Brinkmann (1930), and applied by Jacobsen (1935) for explaining the velocity-range phenomenon in the experiments of Rutherford and Henderson, and also in his own experiments.

The suggestion regarding the occurrence of He^+ and He lines is equivalent to saying that the cloud-chamber phenomena described here occur on the sun on a gigantic scale, but the α -particles are due not to natural radioactive bodies but to some reaction taking place on the solar surface. In the cloud-chamber, some of the α -particles must be capturing electrons in excited orbits, but we

cannot observe emission of the characteristic lines of He, owing to their feebleness. The same is true of the capture of electrons from atoms by He^+ . But in the sun the captures are sufficiently numerous and the lines emitted are strong enough to be observed in the flash. The explanation accounts in a satisfactory manner, at least qualitatively, for the occurrence of $\lambda 4686$ in some strength in the lower chromosphere (up to a height of 2000 km.), and of the occurrence of He lines in the higher chromosphere up to heights of 7500 km., and also their tendency to disappear towards the limb.

There is only one apparent difficulty in this hypothesis of the origin of He^+ and He lines on the sun. According to laboratory observations so far available, the capture of the electron by He^{++} begins to take place when $V \simeq 2c\alpha$, and of the second electron by He^+ when $V \simeq c\alpha$. The He atoms in the sun ought therefore to be in motion with velocities of this order. But this is not apparently observed, though the He lines are actually found broad. The explanation is probably to be found in the fact that α -particles originate below the reversing layer, and by the time they come out of this region they have dissipated most of their energy in the process of ionizing other particles by collision.

If these suggestions stand criticism, it should be possible for us to calculate the intensity of ultra-violet emission from the sun due to He^+ and He, and estimate their relative importance in promoting ionization of the earth's upper atmosphere.

Alpha-particles are produced in many nuclear reactions, and at this stage it is needless to look for any particular reaction which may be mainly responsible for its production on the solar surface. The question is whether α -particles on such vast scales can be produced on the surface of the sun. If so, what is the subsequent fate of these particles? Do they sink deep, get doubly ionized in the interior, and contribute to restoring the α -particle balance of the interior of the sun? These questions may stand for the moment.

It is also worthy of notice that though the visible lines of He are not usually found in the Fraunhofer spectrum, Babcock (1934) records $\lambda 10830$, which is $1s2s\ ^3S-1s2p\ ^3P$ as a faint absorption line in the infra-red part of the Fraunhofer spectrum. This line requires for its production as absorption line some accumulation of He in the $1s2s$ state, which is metastable. This indicates that He exists in some strength in the reversing layer in the normal $1s^2$ and $1s2s$ states, but not in the $1s2p$ or any higher state. The finding is not, in my opinion, antagonistic to the hypothesis of formation of He in the solar atmosphere out of α -particles.

It is obvious that the hydrogen atmosphere of the sun may also originate, at least partly, in the same way, for the proton is also a most frequent product of nuclear reactions. But a hydrogen atom once formed by the capture

of an electron by the proton in the first or, better, in the second orbit can be sustained by radiation pressure, so its career should be fundamentally different from that of the He atom.

It is the belief of the present author that many outstanding problems of the solar and stellar atmospheres, such as prominences, spots, flares giving rise to radio fade-outs, may find their explanation in nuclear reactions taking place more vigorously on limited parts of the surface. It is quite probable that nuclear reactions of the type considered take place more vigorously in the interior, as shown by Bethe (1939) and Gamow (1939), but the probability of their occurrence on the surface on a reduced scale cannot be excluded. For example, it has been found that the He line $\lambda 5876$ occurs as an absorption line in the neighbourhood of disturbed areas, namely, penumbrae of spots. Probably nuclear reactions producing particles are the cause of formation of such disturbed regions, and reactions are much more vigorous than on the normal surface, and a temporary He atmosphere sufficient to give us D_3 in absorption may be formed in these regions.

§2. THE PROBLEM OF THE SOLAR CORONA

Extraordinary interest, in spite of the war, has been aroused in recent years in the problems of the outermost part of the solar atmosphere (inner and outer corona) by the work of Edlén (1942) on the identification of coronium lines. The story of this identification has been told by Russell (1941), by Swings (1943), and by Edlén himself in an exhaustive memoir (1942), and need not be repeated here. It appears to have been conclusively proved that most of the coronal lines are due to atoms of Fe, Ni and Ca which have lost a large number of their outer electrons, sometimes amounting to as many as fifteen or sixteen. The details of this identification, as far as required for our purpose, are given in table 2.

As there appears to be no way of denying the accuracy of the identification, the astrophysicist is faced with a number of problems of a unique type, which may be enumerated as follows:

- (1) What is the physical process giving rise to such highly charged ions?
- (2) How can these highly charged ions, once produced, maintain their charge in the solar atmosphere?
- (3) To explain the other characteristics of these lines noted by Lyot (1939) and in the eclipse expeditions, namely, the great breadth of these lines towards their base, sometimes amounting to $1\text{\AA}$., which gradually diminishes outwards, the intensity variations of these lines, etc., along with phases of solar activity.

These may be called "Coronium problems", in contrast to the second set of problems now to be discussed which

Table 2*

Wave-length (Å)	Intensity		Identification		Ionization potential (ev.)
	Grotrian	Lyot	Ion	Transition	
3328.1	1.0		Ca XII	$^2P_{3/2} - ^2P_{1/2}$	589
3388.10	16		Fe XIII	$^4P_{3/2} - ^4D_{3/2}$	325
3454.13	2.3				
3600.97	2.1		Ni XVI	$^2P_{1/2} - ^2P_{3/2}$	455
3642.87			Ni XIII	$^4P_{1/2} - ^4D_{3/2}$	350
3800.77					
3986.88	0.7		Fe XI	$^4P_{1/2} - ^4D_{3/2}$	261
4086.29	1.0		Ca XIII	$^4P_{3/2} - ^4P_{1/2}$	655
4231.4	2.6		Ni XII	$^4P_{3/2} - ^4P_{1/2}$	318
4311.5					
4359					
4567	1.1				
5116.03	4.3	2.6	Ni XIII	$^4P_{3/2} - ^4P_{1/2}$	350
5302.86	100	120	Fe XIV	$^4P_{1/2} - ^4P_{3/2}$	355
5694.42		1.5			
6374.51	8.1	28	Fe X	$^4P_{3/2} - ^4P_{1/2}$	233
6701.83	5.4	3.3	Ni XV	$^4P_{3/2} - ^4P_{1/2}$	422
7059.62		4			
7891.94		29	Fe XI	$^4P_{3/2} - ^4P_{1/2}$	261
8024.21		1.3	Ni XV	$^4P_{3/2} - ^4P_{1/2}$	422
10746.80		240	Fe XIII	$^4P_{3/2} - ^4P_{1/2}$	325
10797.95		150	Fe XIII	$^4P_{1/2} - ^4P_{3/2}$	325

*Taken from an article by Swings (1943).

may be called the "Corona problems". The two sets of problems must be discussed together as they are complementary. The coronium lines are found to occur in the "Inner corona"—which extends from beyond the top of the chromosphere (height, 14,000 km.), sometimes to a distance of about 10^7 (4.4×10^5 km.) from the photosphere. The inner corona shows, besides the coronium lines a continuous spectrum, which, though nearly a million times fainter, is of the same type as the photospheric spectrum, but with the Fraunhofer lines blurred out. In the outer corona, however, the coronium lines disappear, but the Fraunhofer lines reappear in its continuous spectrum.

The continuous spectrum of the corona has received attention from a number of workers, namely, Minnaert (1930), Grotrian (1933, 1934), and several others. They have proved that it is due to the Rayleigh scattering of photospheric light by an atmosphere of electrons as suggested by Schwarzschild nearly thirty years ago. From the variation of intensity of the coronal light with distance from the photosphere, it is possible to estimate the electron density at different heights, and the figures for a mean corona are reproduced in table 3.

The great difficulty has been to find the source of the electrons constituting the corona. They cannot arise from thermal or photoelectric ionization of solar atoms, as we have then to postulate in coronal heights the existence of a comparable concentration of atoms and ions, which is impossible on dynamical grounds. The best hypothesis appears to be that of Minnaert (1930), and may be given

TABLE 3

*Electron density at various heights in the corona**

h (minutes of arc)	N	h (minutes of arc)	N
0.00	4.58×10^8	22.4	1.79×10^6
0.48	3.11	25.6	1.35
0.96	2.29	28.8	1.10
1.6	1.56	32.0	9.13×10^5
3.2	7.04×10^7	40.0	6.32
4.8	3.84	48.0	5.12
6.4	2.38	64.0	3.81
9.6	1.11	80.0	2.49
12.8	6.13×10^8	112.0	1.63
16.0	3.73	144.0	1.10
19.2	2.50		

*Taken from Unsöld's *Sternatmosphäre*, 1939, chap. 17.

in his own words: "Anderson (1926) has shown that the corona cannot be in equilibrium if the ordinary physical laws are valid. Instead of assuming, as he does, that very hypothetical laws must be applied, we may attempt to account for the corona by assuming that it really is not in equilibrium, and that its particles are continuously being projected towards space."

According to Grotrian (1934), the continuous spectrum of the scattered radiation from the inner corona shows depressions in regions corresponding to chief Fraunhofer absorption lines, but amounting in width to about 100Å., but the lines reappear in the outer corona. He sought to explain the first observation by the hypothesis that the electrons in the inner corona are moving outwards with velocities of the order of 4000 km./sec. According to Moore (1934), the velocity of the coronal streamers (electrons) amounts to 20 to 30 km./sec. These figures probably refer to the outer corona.

Many investigators, including Edlén himself, have sought to explain the occurrence of coronium lines on a temperature basis. The arguments are two-fold:

(1) The coronal lines are, according to measurements of Lyot, quite broad, of the order of 1Å., and if the width be due to Maxwellian motion of the emitting particles, the temperature ought to be 2.34×10^6 °C. This temperature is sufficient to produce the required amount of ionization of the Fe and other atoms.

It is, however, difficult to think of any physical mechanism by which such high temperatures can be produced all over the outer layers of the sun. "Temperature" always means some equilibrium condition, and possibly a small blackbody, placed at the coronal heights, would not show a higher temperature than 3000 to 4000°C. We may, however, have high local temperatures over limited regions, as in the case of a rocket burst in our own atmosphere, where we may have a small region around the rocket in which very high temperatures prevail for a short period of time. Several workers have hinted that the

production of highly stripped iron, nickel and calcium ions responsible for the emission of coronium lines may be due to the bombardment of the solar atmosphere by meteoric matter in the way imagined by Lindemann and Dobson for explaining meteoric flashes in the earth's atmosphere. But the essence of the Lindemann-Dobson theory is that the meteor, striking the earth's atmosphere with a velocity ranging between 7 and 26 km., drives before it the whole column of air in its path, which is heated by adiabatic compression to a temperature sufficient to bring meteoric matter to luminescence. Lindemann and Dobson found that the gas pressure at the heights where

the meteor strikes should be far larger than could be concluded from meteorological considerations. In the sun, the meteoric matter would fall with a velocity of 622 km./sec., but would probably get vaporized long before it reached the chromosphere, and even if some fragments escaped vaporization, the amount of matter in its path would be far too small for production of high temperatures according to the Lindemann-Dobson process. For the meteoric matter which vaporized, the atoms would be rushing with velocities of the order of 622 km./sec. into the solar atmosphere. The effect on these atoms may be obtained by supposing them to remain at rest, and allowing the solar

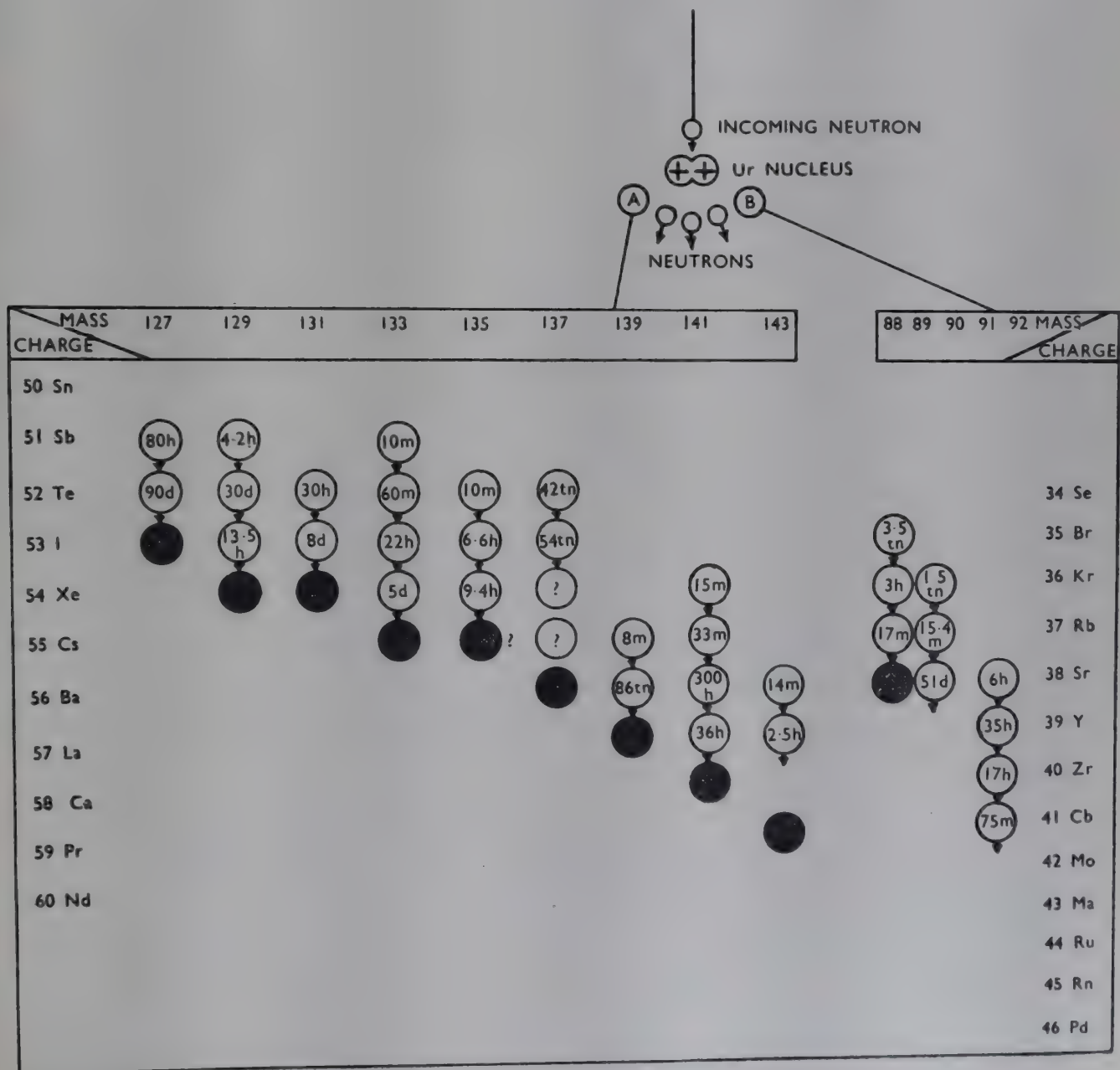
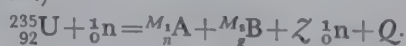


Figure 2.

atoms to rush past them with velocities of the order of 622 km./sec. As far as free and bound electrons are concerned, this is equivalent to bombarding the atoms with electrons having an energy of ≈ 10 volts, which is not sufficient even to tear the outermost electrons from the meteoric atom. As far as the nuclei of solar atoms are concerned, we need take only H nuclei. Their energy is of the order of 5000 volts, and such particles can tear out only one or two outer electrons at each encounter. The meteoric atoms can be deprived of 10 to 14 electrons only when they plunge very deep into the sun, but not at coronal heights. Further, Waldmeier (1938) has shown that the contour of the width curve of the coronal lines as found by Lyot can also be explained on the supposition that the emitters of coronal lines are streaming outwards or inwards with a velocity of 60 km./sec. Lyot (1934) has further found that the width is largest when the emitters are nearest the sun's limb, and becomes narrower as the height increases. This, combined with Waldmeier's suggestion, shows that the emitters of coronal lines are streaming out of the sun with velocities which go on diminishing as greater heights are reached. The meteoric flash theory is not therefore sufficient to explain either the high ionization or the increasing width of coronal lines towards the solar limb, as actually found by Lyot and Waldmeier (1944).

The writer (Saha, 1942) has ventured to suggest that the Fe and other ions responsible for the emission of the coronium lines are due to some nuclear process identical with or akin to that of nuclear fission, discovered by Hahn and Strassmann in 1939. The story of this discovery may be read in several excellent reports on the subject (Livingston, 1941; Walke, 1941), but the facts necessary for astrophysical purpose may be briefly described. It was found by Hahn and Strassmann that when heavy nuclei like ^{238}U , ^{235}U , ^{232}Th , ^{229}Pa are bombarded by neutrons, fast or slow, they break up according to the scheme (for ^{235}U) (figure 2):



${}^{M_1}_x\text{A} + {}^{M_2}_y\text{B}$ are nuclei having respectively the charge numbers x and y , and mass-numbers M_1 , M_2 ; ζ is the number of neutrons, generally 3 or 4, which evaporate in the process (Szilard and Zinn, 1942); Q is the energy evolved in the process.

$$x+y=92, M_1+M_2=236-\zeta.$$

The A products have been found to have x varying from 46 to 60, the B products have y varying from 35 to 46. The reaction is exothermic, as can be seen from mass relationships, and Q is ≈ 200 mev. for binary fission, and it is distributed, according to the law of conservation of energy and momentum, between A and B, A receiving $QM_2/(M_1+M_2)=Q_A$ and B receiving $QM_1/(M_1+M_2)=Q_B$, respectively.

Neither the A nor the B products are stable on account of the high proportion of neutrons, but each has to emit 3 or 4 β -rays successively, till they are reduced to stable forms, as might be illustrated in the chain processes

A	{	Xe $\rightarrow$	β Cs $\rightarrow$	β Ba $\rightarrow$	β La $\rightarrow$	β Ce (stable)
$M=141$		54	55	56	57	58
			15m	33m	300h	36h
B	{	Sr $\rightarrow$	β Y $\rightarrow$	β Zr $\rightarrow$	β Nb $\rightarrow$	β Mo (stable)
$M=91$		38	39	40	41	42
			8h	38m	17h	75m

The fission process is beautifully illustrated in the Wilson-chamber photographs taken by Corson and Thornton (1939), Böggild *et al.* (1941) in Prof. Bohr's laboratory before Denmark was invaded.

What is important for our purpose is the high energy with which the fission fragments are thrown out in the reaction. To take an example: If $x=54$, $M_1=141$, $y=38$, $M_2=91$, $\zeta=4$, we have $Q_A \approx 80$ mev. and $Q_B \approx 120$ mev. The velocities corresponding to these energies are $V_A \approx 4.7 c\alpha$, $V_B \approx 7.1 c\alpha$. These velocities are much larger than the orbital velocity not only of the outer electrons of the stable products, but also of many of their inner electrons. Bohr (1941), Knipps and Teller (1941) and Lamb (1941) have pointed out that as soon as the fission fragments are produced in any medium, they lose most of their outer electrons and can retain only those of their inner electrons whose orbital velocities are larger than, or comparable to, their own velocity. The fission particles therefore start as heavily ionized ones bereft of a large number of their outer electrons, and Bohr and Wheeler (1939) quote a Russian worker, Perlov (?), as having experimentally proved that the charge may be as high as 20.

The presence of Fe or Ni amongst the fission fragments has not yet been reported with definiteness, but considerations of energy and probability do not rule them out. Nishina and his co-workers (1939) have shown that the probability of a symmetric fission in which one fragment is much larger than the other increases with the energy of the bombarding neutrons. Further, ternary and quaternary fission are allowed by considerations of energy and probability, and Q in some cases may be as high as 250 mev., which is larger than the 200 mev. maximum energy evolved in the binary fission process. It may be supposed that as a result of either of such processes taking place in the sun, smaller fragments are produced which, after a number of β -emissions, ultimately stabilize as nuclei of elements from Ca to Ni and are emitted with energies of the order of 60 mev. It is gratifying to note that after the writer had postulated such a process for the origin of coronal emitters, ternary and quaternary fission were reported by Lark-Horowitz (1941) and theoretically treated by Present (1941).

TABLE 4*

STRIPPED IRON IONS AND THEIR ELECTRON STRUCTURE, ETC

Ion	Electron structure	Fundamental state	Value of the lowest terms in volts	$\sqrt{\frac{I.P.}{13.54}} = \frac{z_i}{n}$	Remarks
$^{26}\text{Fe I}$	..3d ⁶ 4s ²	⁵ D ₄	7.83	0.76	Forbidden lines found in η Carinae. Bowen (1936).
Fe II	..3d ⁶ 4s	⁶ D _{9/2}	16.5	1.10	
Fe III	..3d ⁵	⁶ D	30.48	1.50	Bowen (1940) gives metastable lines found in nebulae. D. Kundu thinks that some of these lines may occur in the corona.
Fe IV	..3d ⁴	⁶ S	56.8	2.05	
Fe V	..3d ⁴	⁵ D ₀	..	(2.37)†	
Fe VI	..3d ³	⁴ F _{3/2}	..	(2.69)	
Fe VII	..3d ²	³ F	..	(3.01)	" " "
Fe VIII	..3d	² D	150.4	3.33	
Fe IX	..3p ⁶	¹ S ₀	233.5	4.15	No metastable state.
Fe X	..3p ⁵	² P	261	4.39	
Fe XI	..3p ⁴	³ P	288.9	4.62	λ 6374.75 ² P _{3/2} ← ² P _{1/2} . λ 7892
Fe XII	..3p ³	⁴ S	320	(4.91)	
Fe XIII	..3p ²	³ P ₀₁₂	346	(5.06)	{ 10746.80. 10797.95. λ 5303 ² P _{1/2} ← ² P _{3/2} . No metastable state.
Fe XIV	..3p	² P	373	5.25	
Fe XV	..3s ²	¹ S ₀	454	5.79	" "
Fe XVI	..3s	² S _{1/2}	487	5.99	
Fe XVII	..2p ⁶	¹ S ₀	1259.7	9.65	" "

*Reproduced from the author's paper, "On a physical theory of the solar corona," *Proc. Nat. Inst. Sci.* **8**, 99, (1942).

†Parentheses () denote that the value is extrapolated.

It can be shown that if one of the heavy fission-elements undergoes a ternary or a quaternary fission, the fragments, after a number of β -emissions, will be elements from Ca to Ni (the limit on both sides is rather elastic), and they will be emitted with an energy of approximately 60 mev., i.e., in the case of Fe atoms with a velocity of 6.4 $c\alpha$. Let us now turn to table 4, which shows the velocity of the outermost electrons of iron, and its ions. We find that the 2 p -electron of Fe xvii has a velocity of 9.6 $c\alpha$. This will therefore be retained, but if we take Fe xvi, the 3s-electron is found to have a velocity of 6 $c\alpha$. We can therefore conclude that in a fission process of the type envisaged here, occurring in the reversing layer, the iron atoms which normally have the electron composition 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁶ 4s² will have lost the outer 15 electrons, namely, 3s 3p⁶ 3d⁶ 4s², and will start as Fe xvi with the electron composition 1s² 2s² 2p⁶ 3s. It will now be interesting to follow the physical processes to which such a highly charged ion produced anywhere in the sun can give rise, as it passes through the solar atmosphere. These are:

(a) *Ionization by collision.* The ion goes on knocking electrons and nuclei from the atoms which it encounters in its way, just as an α -particle does when it is projected in a cloud-chamber. In this process, the ion continuously loses energy, and it is possible to calculate its range with the aid of the Bohr-Bethe formula (1936), provided we assume

that the solar atmosphere consists mainly of H atoms with few C and N atoms (as given by Menzel). The range is found on certain plausible assumptions to be $R_H \simeq 1.31 \times 10^{21}$ H atoms/cm.² for Fe xvi projected with a velocity of 6.4 $c\alpha$.

We can draw very important conclusions from this calculation. Nuclear processes giving rise to Fe xvi, or similar highly charged iron or other ions may occur throughout the whole *solar interior*, but most of such particles have no chance of ever passing out of the solar atmosphere. Most of them will stop dead earlier. If the number of H-particles in the reversing layer is taken to be 1.8×10^{22} /cm.² (Unsöld, 1939), R_H is far less than this number, and it is obvious that only those fission particles which are produced rather high up in the "reversing layer" have a chance of escaping through the chromosphere and emerging into the inner corona.

(b) *Possibility of the further loss of an electron by the ion.* The Fe ion may itself lose a further electron by collision with atoms, but the probability of this event vanishes when the velocity of the ion reaches a certain limiting value. For the solar atmosphere, the limiting velocity, under certain plausible assumptions, is $V_c \simeq c\alpha.z$, where z is the net charge on the ion. The Fe xvi ion cannot therefore lose any further electron.

(c) *Capture of electrons by the ion.* The Fe xvi may capture

an electron from any one of the atoms in its path, or even a free electron, and become Fe xv: $1s^2 2s^2 2p^6 3s^2$ (normal) or $3s nx$, where nx is a higher orbit. The probability of the capture at first increases as the velocity of the ion diminishes. When the capture is in an excited orbit, the iron is expected to execute one or more quantum transpositions, emitting x rays, and ultimately we shall have normal Fe xv. This has no metastable levels, so no visible radiation can be emitted by Fe xv.

The Fe xv ion will now pass through the same career as Fe xvi, but the electron composition of the next ion formed is $1s^2 2s^2 2p^6 3s^2 3p$, and hence we have two metastable levels, $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$. The strong coronal line $\lambda 5303$ is due to the forbidden transition $^2P_{\frac{3}{2}} \rightarrow ^2P_{\frac{1}{2}}$. The emission of $\lambda 5303$ necessarily indicates that some amount of x radiation due to the allowed transition $3s^2 nx \rightarrow 3s^2 3p$, $\lambda \approx 80\text{\AA}$, is also being emitted. The capture can take place at all velocities of Fe xv, from $s=6$ down to $s=0$, but the formula of Brinkmann and Kramers has been worked out only for capture in S -orbits and for high velocities of the ion. It has still to be worked out for small s and for capture in p -orbits; hence at this stage it is not possible to give any quantitative estimate. The next ions from Fe xiv to Fe x are all formed by successive capture of electrons from the solar atoms or of free electrons in the solar atmosphere, and thus the $3p^x$ -shell is formed ($x=1$ to 5), which gives us the coronal radiation given in table 2.

The possibility of any one of the Fe xiv to Fe x ions emerging out of the chromosphere to the coronal heights therefore depends upon: (i) the probability of a fission of the type mentioned above taking place in the sun, (ii) the region where the fission takes place. Bohr and Wheeler (1940) have shown that only heavy nuclei like ^{238}U , ^{235}U , ^{232}Th , ^{229}Pa are capable of fission. These can occur in the solar interior as well as in the reversing layer, but ions formed in the interior are stopped dead earlier, and only such as originate in the reversing layer can escape to coronal heights. The origin of the coronium emitters is therefore to be found in the upper part of the reversing layer.

At this stage some of the probable doubts and objections in the mind of the reader may be anticipated:

(1) Have we in the sun's atmosphere or interior sufficient U or Th atoms, which alone have been shown by Bohr and Wheeler (1939) to be capable of fission by neutron-bombardment?

U has not yet been traced in the sun, probably owing to the extreme complexity of its spectrum. But the presence of lines of singly-ionized Th has recently been definitely established by Moore and Babcock (1943).

(2) Why should we get only Fe, Ni and Ca in the corona, and not any of the contiguous elements, say Co, Mn, or Cu, A or K?

An investigation carried out by D. Kundu (1942) at

Calcutta shows that Fe, Ni and Ca are spectroscopically better suited for identification than any other elements in this group excepting Co. But Co is probably represented by a faint line in the corona, $\lambda 4359$, which Kundu attributes to Co xv. Subsequently, through the courtesy of the Astronomer Royal of England, the writer has been able to have access to a copy of Edlén's paper (1942) in which the same opinion has been expressed.

But even if Co, Mn and other elements of the group are subsequently found to be represented by some of the fainter coronal lines not yet identified, it is clear that these elements are represented far less strongly than Fe, Ni and Co. Edlén has tried to connect the phenomenon with the so-called cosmic frequency of elements. But probably the real reason is that in a nuclear process there is a greater probability of the occurrence of even-numbered atomic elements than of odd-numbered ones. Each one of the former is represented by four or more isotopes, but the latter generally (for example, Sc, V, Mn and Co) by a single isotope. There is, therefore, a greater chance of fission products ultimately transforming themselves after β -emissions to Fe, Ni and Ca than to Co, Mn and Sc.

(3) Why do we not observe the forbidden lines of Fe ions from Fe ix to Fe ii, and of the corresponding ions of Ni, amongst the coronium-lines?

Fe ix has no metastable state and Fe viii has the composition $1s^2 2s^2 2p^6 3s^2 3p^6 3d$. The ($3d\ ^2D_{\frac{3}{2}} - ^2D_{\frac{5}{2}}$) separation is too small to give a line in the visible range. Some of the forbidden lines of Fe vii to Fe iii having the composition of $3d^x$ have been traced by Bowen in the nebulae, and of Fe ii in η Carinae, and by Merrill (1943) in BF Cygni and other stars; Kundu thinks, too, that some forbidden lines of Fe v can be identified with fainter, doubtful lines in the solar corona. But these doubtful lines require further investigation, both as regards wave-length measurements and identification.

It is clear that even if subsequent investigations prove that the forbidden lines of the $3d^x$ -complex (Fe viii to Fe ii) occur in the corona, they would prove to be extremely faint compared to the forbidden lines of the $3p^x$ combination. This may be due partly to the fact that the probability of capture of an electron in a d -orbit is far smaller than that in a p -orbit. Exact calculations are difficult and are being carried out, but the finding is questionable.

The complete establishment of these ideas will require a colossal amount of experimental and theoretical investigations, the nature of which is clearly indicated in the text. But the value of the hypothesis can also be assessed from a discussion of its bearing on the associated problems of the solar corona mentioned earlier.

If the considerations presented here regarding the origin of emitters of coronium lines prove to be correct, it is obvious that the electrons constituting the inner and outer corona are simply the δ -rays liberated by the

coorinium-emitters (Fe xiv and others) from H and other atoms in the upper reversing layer, and the chromosphere in the process of ionization by collision as these highly charged emitters of coronium lines pass through the solar atmosphere. The velocity of these electrons is given by the relation $V_e = 2V_i \cos \phi$, where V is the velocity of the ion and ϕ the angle between the direction of emission of the δ -electron with the original direction of motion of the ion. It is clear that $V_e \approx 2V_i \approx 2c\alpha$, and may have as high values as $2c\alpha$. The swifter electrons are mostly emitted inside the reversing layer and inside the chromosphere, and will be able to escape with velocities of the order $2c\alpha$; they probably constitute the electron atmosphere which we know as the corona. The theory has evidently to be further worked out to yield more details about the corona.

The coronal problems are almost unique in astrophysics, because if we leave out the sun, the coronal lines are not observed in the very wide range of astrophysical phenomena; neither in spectra of normal or peculiar stars, nor in those of novae or supernovae, except in the solitary case of recurrent novae (RS Ophiuchi), as was discovered by Adams and Joy (1933), and confirmed by Swings and Struve (1943). But it is inconceivable to think that the sun should be a solitary exception. Probably the same physical processes which give rise to coronal lines are occurring everywhere, but the scale, compared with those of ordinary stellar emission, is far too low for the lines to be observable. We are able to observe them on the sun merely on account of our proximity to this star, and that only on special occasions (time of total eclipse) or by special devices (Lyot).

Is it possible to give more definiteness to the question of the *scale* of coronal emission compared to those of ordinary photospheric or chromospheric emissions? The photosphere emits 1500 cal./sec. per cm.² of its area, the chromospheric emissions in H α come to about $\frac{1}{50}$ of the corresponding photospheric emission in H α , and according to estimates of Lyot, the coronal emission in the green line is of the order of 10^{-6} A. of the corresponding photospheric emission.

The ideas presented in this lecture may be compared with those of Rosseland (1934):

"Considering, for instance, the most familiar case, that of the sun, it is surprising how few theories are of such an obvious character as to deserve unreserved applause. It will probably be admitted generally that the interpretation of the origin of Fraunhofer lines is now so far advanced that a revision of fundamental principles may be unnecessary in this field. Proceeding a little further to the interpretation of spectroheliograms, the ground is already getting considerably more insecure. And when we proceed still further, we meet the enigmas of the sunspots, the prominences, the chromosphere, and the corona, none of

which can at present be said to be understood, even in the most liberal interpretation of the term.

"The enigmatic character of these phenomena is not so much concerned with the generally admitted fact that we do not understand their common cause, which underlies solar activity as a whole. It is more that we do not know how to interpret the individual manifestations in an intelligible manner. We know of no simple mechanism at present according to which magnetic fields of the magnitude observed in sunspots could be generated. The motion of prominences is recognized as quite different from any motion which could be produced by the combined action of gravitation and electromagnetic forces on a mass of gas in a vacuum, and the agglomeration of matter in the corona surpasses by billions the amount to be expected on any simple hydrostatic theory. These various facts have stimulated speculation to the breaking point, it being even suggested that here we witness our recognized physical laws set at naught by nature herself. Although these speculations are not likely to be taken very seriously by the experienced physicist, they bring out forcibly the unsatisfactory state of solar theory today."

Rosseland's view in 1934 was: "Chromosphere, corona and prominences would in that case form a complex of dynamic phenomena, the theory of which must be based on considerations of the expansive motion of matter moving away from the sun in a more or less radial direction. It does not follow, of course, that all matter in a streamer is moving with the same velocity."

Rosseland concludes: "Though we definitely do not know the nature of these primary particles, the existence of which is indicated by general arguments, there are reasons to believe that they are electrically charged."

Rosseland has considered the equilibrium (?) of the electrified atmosphere, but the physical factors introduced (for example, resistance to the motion of positively and negatively charged particles) are of a vague character. Probably the ideas introduced here will impart definiteness to these factors.

The idea of temperature-equilibrium can be applied to the photosphere and the reversing layer, and that, too, very approximately. The general chromospheric phenomena and other associated ones like prominences are probably partly due to temperature, partly to radiation pressure, and probably nuclear reactions giving rise to α -particles and protons play some part. The coronal phenomena are of a different type—arising from a process akin to or identical with fission, and they are just like rocket-bursts in our atmosphere. The three types of phenomena intermix and produce a complicated picture.

The author had the privilege of discussing the theory of the corona given here with Professor Dirac during a short visit to Cambridge. Dirac made the most interesting suggestion that the β -rays emitted by the fission products

may turn out to be the high-energy electrons which are wanted for explaining auroral phenomena. For it is well known that Störmer's theory of the aurora has not been able to explain why the zone of maximum frequency of the aurora is at a distance of 22° from the magnetic poles (see Hewson, 1937). This proves that the corpuscular rays responsible for the auroral phenomena cannot be photo-electrons, or even β -rays of moderate energy. They can be either β -rays of energy of the order of 5 to 10 mev. or α -particles, but the last possibility is generally ruled out on other grounds. The β -rays expected to be given out by fission products have the requisite energy, but there are other factors, and the problem may be left at this stage.

This article was prepared in course of the author's tour through England and U.S.A., in 1944-1945 on a Government of India Mission, and he had the pleasure of discussing its contents with many friends, to whom his grateful acknowledgments are due. He is particularly indebted to Dr. J. A. Fleming, director of the Geophysical Institute, Washington, D. C., and Mr. Allan Shapley for unstinted help in the final preparation of the manuscript.

REFERENCES

- ADAMS and JOY, 1933. "Spectrum of RS Ophiuchi." *Pub. Astr. Soc. Pacific*, **45**, 301.
- BABCOCK, 1934. "He lines in the Sun." *Pub. Astr. Soc. Pacific*, **46**, 132.
- BETHE, 1939. "Energy-production in stars." *Phys. Rev.* **33**, 434.
- BÖGGILD *et al.*, 1941. "Range and straggling of fission-particles." *Phys. Rev.* **59**, 275.
- BOHR, 1940. "Scattering and stopping of fission fragments." *Phys. Rev.* **58**, 659.
- BOHR and WHEELER, 1939. "Mechanism of nuclear fission." *Phys. Rev.* **56**, 426.
- BRINKMAN and KRAMERS, 1930. "Capture of electrons by α -particles." *Proc. K. Akad. wet. Amst.* **33**, 973.
- CORSON and THORNTON, 1939. "Disintegration of uranium." *Phys. Rev.* **55**, 509.
- EDLÉN, 1942. "On the identification of coronal lines." *Z. Astrophys.* **22**, 30.
- GROTRIAN, 1933. "Variation of intensity of coronal lines." *Z. Astrophys.* **7**, 26.
- HEWSON, 1937. "A survey of the facts and the theories of the aurora." *Rev. Mod. Phys.* **9**, 403.
- JACOBSEN, 1935. "Capture of electrons by swift α -particles." *Phil. Mag.* **10**, 401.
- KNIPPS and TELLER, 1941. "Energy loss of heavy ions." *Phys. Rev.* **59**, 659.
- LAMB, 1941. "Passage of uranium fragments through matter." *Phys. Rev.* **58**, 596.
- LARK-HOROVITZ and SCHREIBER, 1941. "U fission with Li-D neutrons." *Phys. Rev.* **60**, 156.
- LIVINGSTONE and BETHE, 1937. "Report on nuclear physics." *Rev. Mod. Phys.* **9**.
- LYOT, 1939. "Study of the solar corona and prominences." *Mon. Not. Roy. Astr. Soc.* **99**, 580.
- MERRILL, 1943. "The spectrum of F-Cygni." *Astrophys. J.* **98**, 473.
- MERRILL, 1944. "Spectroscopic observations of α Persei, etc." *Astrophys. J.* **99**, 481.
- MINNAERT, 1930. "Continuous spectrum of the corona." *Z. Astrophys.* **1**, 209.
- MOORE and BABCOCK, 1943. "Thorium in the Sun." *Pub. Astr. Soc. Pacific*, **55**, 22.
- NISHINA *et al.*, 1939. "Fission of thorium by neutrons." *Nature, Lond.*, **144**, 547.
- OPPENHEIMER, 1928. "Quantum theory of capture of electrons." *Phys. Rev.* **31**, 349.
- PANNEKOEK and MINNAERT, 1928. "Observations of solar lines, etc." *Proc. K. Akad. wet. Amst.* **13**.
- PEREPELKIN and MELNIKOV, 1935. *Publications of the Pulkowa Observatory*, no. 122, 14.
- PRESENT, 1941. "Possibility of ternary fission." *Phys. Rev.* **59**, 467.
- ROSSELAND, 1933. "On the theory of the chromosphere and the corona." *Proc. Oslo Akad.*
- RUSSELL, 1941. "A puzzle solved." *Scientific American*, **165**, 70.
- RUTHERFORD, 1924. "Capture and loss of electrons by α -particles." *Phil. Mag.* **47**, 277.
- SAHA, 1921. "On a physical theory of stellar spectra." *Proc. Roy. Soc. A*, **99**, 135.
- SAHA, 1942. "On a physical theory of the solar corona." *Proc. Nat. Inst. Sci. India*, **8**, 99.
- SWINGS, 1943. "Edlén's identification of the coronal lines, etc." *Astrophys. J.* **98**, 116.
- SWINGS and STRUVE, 1943. *Astrophys. J.* **97**, 204.
- TURNER, 1940. "Nuclear fission." *Rev. Mod. Phys.* **12**, 1.
- UNSÖLD, 1939. *Sternatmosphäre*.
- WALDMEIER, 1937. "On the significance of contours of corona-lines." *J. Astrophys.* **15**, 44.
- WALDMEIER, 1944. "Observations of corona before and after total solar eclipse, etc." *J. Astrophys.* **20**, 250.
- WALKE, 1940. *Rep. Progr. Phys.* **6**, 16.

77. ON NUCLEAR ENERGETICS AND BETA-ACTIVITY

M. N. SAHA AND A. K. SAHA

(*Trans. Nat. Inst. Sci. Ind.*, **2**, 193, 1946)

Received April 9; read April 17, 1946.

ABSTRACT

The following is an attempt to discover regularities in the energetics of the β^+ , β^- and γ -emissions, and of K -capture of different nuclei. It follows an earlier attempt by the senior author, S. C. Sirkar and K. C. Mukherjee (1940) to find out empirical rules of stability of nuclei. The authors have deduced, from the Weizsäcker-Bethe formula, expressions for energy-release in the case of β -transitions and K -capture, which involve only the isotopic number term, the coulomb-interaction terms, and spin-dependent terms in the mass-defect formula. The nuclei have been classified into group having a definite value of I , and the theoretical results have been compared to the observed ones. Generally good agreement has been obtained in the case of nuclei belonging to the seven groups $I = -1$ to $I = 6$ whose properties are well determined. A few glaring anomalies have been pointed out, e.g. Ca^{48} announced as a rare stable isotope of calcium by Nier, cannot possibly exist as a stable nucleus. This has also been pointed out by I. Curie. Many apparent anomalies from empirical rules of stability have been explained. The present work covers all nuclei from $I = -1$ to $I = 6$, and further work is contemplated.

INTRODUCTION

Ever since the discovery by the Joliot-Curies of the phenomenon of induced radioactivity, a very large number of radioactive nuclei (exceeding 400) has been prepared in the laboratory in addition to those existing naturally. In recent years, new types of radioactive nuclei have been obtained from fission of heavy nuclei like U, Th and Pa. The data so far collected in the different laboratories of the world form a rather bewildering mass, as can be easily seen from a glance at the comprehensive tables of isotopes given by Turner (1940), Livingood and Seaborg (1944) and Seaborg (1944). In many cases, the designation of a new isotope by mass is not quite unambiguous; indeed this is a very acute problem for fission products.

Several attempts at a regularisation of data have been made by previous workers, but we may start with a paper by Saha, Sirkar and Mukherjee (1940) where references to previous works will be found. In the present paper the notation used in the previous work will be employed, but it is repeated in order to spare the reader the trouble of constantly looking back for reference.

The chart of atomic nuclei—The essence of the paper by Saha *et al.* is a comprehensive chart of atomic nuclei, hereinafter called the Nuclear Chart. A section of it is shown in Fig. 1. In this the abscissa represents mass-number A , the ordinate represents the isotope number $I = N - Z$, which represents the excess of neutrons over protons in any nucleus. A ranges from 1 to 239, and I from -1 to about 54. The section of the chart reproduced here extends from $I = -1$ to $I = 8$. We have attempted to make the

chart as up-to-date as possible. The parallel lines at 45° to be henceforth called the Z -lines, represent the atomic number Z . Thus all isotopes of the element Z are to be found on the same Z -line. Each isotope is represented by a circle. Solid circles ($\bullet$) represent 'Stable nuclei'. Hollow circles (δ) with an arrow pointing upwards represent β^+ (positron) emitting nuclei. When the arrow points down (φ), it indicates that the nucleus is β^- (electron) emitting. Circles with arrows pointing both up and down like ϕ indicate that the nucleus emits both negatrons and positrons, e.g. Cu^{64} . δ denotes that the nucleus decays by K -capture only. ϕ denotes that the nucleus decays by K -capture as well as by positron-emission. φ denotes that the nucleus has been obtained in 'fission'; such nuclei are all β^- -emitting. If any particular isotope has two different half-lives (isomers), both half-lives are given (cf. Co^{60}). Saha, Sirkar and Mukherjee (1940) gave the following rules of stability, some of which have been previously known.

Rule 1.— $I = \text{even}$: When I is even, say 4, we get alternation of stable and β -active nuclei. All even-even nuclei having $Z = \text{even}$, $N = \text{even}$ are stable. All odd-odd nuclei ($Z = \text{odd}$, $N = \text{odd}$) are unstable. This rule has also been given by Bethe and Bacher (1936). Exceptions are (a) for even-even nuclei: He^6 , Be^{10} , C^{14} , Pb^{210} (RaD) which are all β^- -emitting, (b) for odd-odd nuclei: H^2 , Li^6 , B^{10} , N^{14} which are all stable.

Rule 2.— $I = \text{odd}$: If in any of the odd groups, we arrange the nuclei in order of their mass-number, we first find β^- -active nuclei, then arrive at a number of succeeding

stable nuclei, which are followed by nuclei decaying by β^+ -emission or K -capture. The number of stable nuclei in any group has been found sometimes as large as 13, and sometimes as small as 3. There are a few exceptions to this rule which will be mentioned in proper places.

These rules apply only to known nuclei. Supposing for any particular I , say $I=4$, which starts from P^{34} and ends at Ga^{66} , the membership is extended on both sides. Would they continue to obey this rule? Would Na^{20} , Al^{30} , Si^{32} , As^{70} , Br^{74} , and Rb^{78} , etc. which are at present unknown be found stable when they are made in the laboratory or would they be unstable?

In this paper, attempt has been made to obtain an explanation of the above rules and at a quantitative expression for the energy-release of β -emission of nuclei.

§1. NOTATION AND FORMULAE USED

Let us now explain the notation and formulae used for explaining the empirical rules of stability, and further, as we shall see, for arriving at some regularity in the nature of β -emissions. We use the following symbols:—

${}_Z M^A$ = mass of the bare nucleus ' M ' with mass-number A and atomic number Z .

$M(Z, A)$ = mass of the full-atom (i.e. of the nucleus plus the Z -electrons),

$$= {}_Z M^A + Zm. \quad \dots (1.1)$$

Energetics of β -emission:

(A) β^- -emission—A nucleus ${}_Z M^A$ when emitting a β^- -particle, and transforming to ${}_{Z+1} M^A$ will release the energy E^- given by

$$E^- = {}_Z M^A - {}_{Z+1} M^A - m = M(Z, A) - M(Z+1, A) \dots (1.2)$$

This energy E^- is the total energy released in the β^- -transition, i.e. it is the sum of the end-energy of the liberated electrons and the total sum of the energies of the γ -rays genetically connected with these electrons.

(B) β^+ -emission—A nucleus ${}_Z M^A$ when emitting a β^+ -particle and transforming to ${}_{Z-1} M^A$ will release a total amount of energy E^+ given by

$$E^+ = {}_Z M^A - {}_{Z-1} M^A - m = M(Z, A) - M(Z-1, A) - 2m. \quad (1.3)$$

(C) K -capture—The K -capture phenomenon was first discovered by Alvarez (1938) and its theory was earlier given by Yukawa and Sakata (1935) and independently by Möller (1937). An account is included in the report on β -decay by Konopinski (1943). When a K -electron is captured by a nucleus ${}_Z M^A$, it changes to ${}_{Z-1} M^A$ and the total energy released E^K is given by

$$\begin{aligned} E^K &= {}_Z M^A + m(1 - \alpha^2 Z^2)^{\frac{1}{2}} - {}_{Z-1} M^A, \\ &= M(Z, A) - M(Z-1, A) - m\{1 - (1 - \alpha^2 Z^2)^{\frac{1}{2}}\}. \quad (1.4) \end{aligned}$$

Here $m(1 - \alpha^2 Z^2)^{\frac{1}{2}}$ represents the total mass of the captured K -electron, according to Dirac. Combining (1.3) and (1.4) we observe that if

$$2m > M(Z, A) - M(Z-1, A) > m\{1 - (1 - \alpha^2 Z^2)^{\frac{1}{2}}\} \simeq m\alpha^2 Z^2, \quad (1.5)$$

for light elements, then only K -capture will take place. But if

$$2m < M(Z, A) - M(Z-1, A), \quad \dots (1.6)$$

K -capture as well as positron-emission may take place. In fact there is a competition between the two processes. As the difference $M(Z, A) - M(Z-1, A)$ becomes larger and larger than $2m$, positron-emission predominates over K -capture. The point has been discussed in detail by Konopinski (1943).

To obtain the exact value of E^+ , E^- , and E^K we have to know the value of the masses $M(Z, A)$, $M(Z+1, A)$, $M(Z-1, A)$ correctly. The empirical method of doing so is to measure the atomic mass correctly in the mass-spectrograph, as has been done by Aston and others. These workers express the exact value of $M(Z, A)$ in terms of a packing fraction f defined by

$$f = \frac{M(Z, A) - A}{A}, \text{ i.e. } M(Z, A) = A(1 + f). \quad \dots (1.7)$$

Tables of $M(Z, A)$ and f are given by Aston (1942), Dempster (1936), Mattauch and Flüge (1942), Graves (1939) and Duckworth (1942).

Though f has been determined for a large number of nuclei, there are many important gaps and some of the older determinations have to be revised. The masses of radioactive nuclei have to be obtained from the energetics of reactions used to produce them.

Binding energy of nuclei.—The binding energy of a nucleus ${}_Z M^A$ is given by

$$\Delta M(Z, A) = NM_n + ZM_p - {}_Z M^A = (0.00853 - f)A + 0.0004I. \quad (1.8)$$

Thus whenever the packing fraction is given, we may calculate the binding energy $\Delta M(Z, A)$ for the formation of a nucleus out of Z -protons and N -neutrons.

The binding energy formula based on the classical liquid drop model.—Several semi-empirical formulae for binding energy have been given. We have used in this paper the formula used by Bethe (1936) which is a modified form of one first introduced by Weizsäcker (1935), and we have added to it a term $\chi(Z, A)$ presently to be explained. The formula is

$$\Delta M(Z, A) = \phi(Z, A) + \chi(Z, A), \quad \dots (1.9)$$

where $\phi(Z, A)$ is the part due to Weizsäcker and Bethe, viz.

$$\phi(Z, A) = \alpha A - \beta \frac{I^2}{A} - \gamma A^{\frac{2}{3}} - \delta \frac{Z^2}{A^{\frac{1}{3}}}. \quad \dots (1.10)$$

1
2
3

4

5
6

7
8
9
10
11

12
13

14

15
16
17
18
19
20

It is known empirically that $\Delta M(Z, A) = \phi(Z, A)$, i.e. $\chi(Z, A) = 0$ only for even Z , and even N for which the nuclear spin i is generally zero. All other nuclei have finite spin. For them $\chi(Z, A)$ will be finite. We shall call $\chi(Z, A)$ the spin-dependent part of nuclear binding energy. Usually this part was neglected as being too small compared to the other terms in the mass-defect formula. Our work will show, however, that this term, although negligible compared to the other terms in the binding energy formula, viz. $(\alpha A, \gamma A^{\frac{2}{3}})$, being of the order of 3 Mev in most cases, grows in importance when one applies the binding energy formula to explain the energy-release in β -decay processes, for the terms $\alpha A, \gamma A^{\frac{2}{3}}$ cancel out.

It is also known that a nucleus may have different values of spin i , in other words $\chi(Z, A)$ may be *multivalued*. This brings us to the question of nuclear levels and isomeric states which will be taken up later.

The spin-independent part of $\Delta M(Z, A)$ contains four constants

$$\alpha, \beta, \gamma, \delta.$$

Of these only δ is known from theory with certain amount of definiteness. It is given by

$$\delta = \frac{3}{5} \frac{e^2}{r_0}, \text{ where } r_0 = \text{a nuclear constant} \simeq \frac{e^2}{m_0 c^2}.$$

The other constants are obtained in such a way that $\Delta M(Z, A)$ calculated from the Weizsäcker-Bethe formula fit with the experimental values. For details, see Bethe and Bacher (1936). Bethe gives the following values for the mass-defect constants

$$\alpha = 13.86 \text{ Mev}, \beta = 19.5 \text{ Mev}, \gamma = 13.2 \text{ Mev}, \delta = .58 \text{ Mev}.$$

It should be noted, however, that he took the neutron and proton masses to be 1.00845 MU and 1.00807 MU respectively. Repeating his calculations with the more recent values of the masses, viz. $M_n = 1.00893$ MU and the mass of H^1 atom = 1.00813 MU we get

$$\alpha = 14.058 \text{ Mev}, \beta = 18.9 \text{ Mev}, \gamma = 13.08 \text{ Mev}, \delta = .58 \text{ Mev}.$$

In what follows we have, however, taken $\beta = 19.5$ Mev for it will be clear from subsequent discussions that for the groups at the beginning of the nuclear chart we need a value of β much greater than 18.9 Mev to explain the experimental facts. However, it is possible that for the groups $I=6$ and groups beyond it, $\beta = 18.9$ Mev, the standard value, will explain better the β -activity of the different members of these groups.

There are other mass-defect formulae, e.g. those due to Wigner (cf. Wigner and Feenberg, 1941), which has been used by Barkas (1939) in an attempt to obtain a finer analysis of nuclear binding energies. Probably by using these formulae, our results for energy-release would be improved, but we have not tried to use these formulae,

as they are very complicated. We have, however, pointed out the defects arising from our formula in relevant places.

The masses and binding energies can be expressed in terms of either

- (a) Mass units or millimass units.
- (b) Electron volts.
- (c) Units of $m_0 c^2$ (electron rest mass units).

We use the following conversion table:—

$$1 \text{ mMU} = .9317 \text{ Mev}.$$

$$1 \text{ electron rest energy unit} = .000549 \text{ MU} = .5112 \text{ Mev}.$$

$$1 \text{ Mev} = 1.074 \text{ mMU}.$$

We have made use of Birge's (1941) summary of the general physical constants.

§2. TOTAL ENERGY-RELEASE IN β -EMISSION

Let us now obtain values of E^- , E^+ , and E^K . We have from (1.2)

$$E^- = M_n - M_p - m + \Delta M(Z+1, A) - \Delta M(Z, A).$$

Now using the mass-defect formula (1.9), it can be easily shown that

$$E^- = A^- + \chi(Z+1, A) - \chi(Z, A), \quad \dots (2.1)$$

where A^- is the spin-independent part, being given by

$$A^- = M_n - M_p - m + \frac{4\beta(I-1)}{A} - \frac{\delta(A-I+1)}{A^{\frac{1}{2}}}. \quad \dots (2.2)$$

In million electron volts, we have

$$A^- = .766 + \frac{78(I-1)}{A} - \frac{.58(A-I+1)}{A^{\frac{1}{2}}}, \quad \dots (2.3)$$

where we have generally taken for β the value given by Bethe, viz. 19.5 Mev.

In a similar way, we have, for the energy-release in positron-emission

$$\begin{aligned} E^+ &= -M_n + M_p - m + \Delta M(Z-1, A) - \Delta M(Z, A), \\ &= A^+ + \chi(Z-1, A) - \chi(Z, A), \end{aligned} \quad \dots (2.4)$$

$$\text{where } A^+ = -M_n + M_p - m - \frac{4\beta(I+1)}{A} + \frac{\delta(A-I-1)}{A^{\frac{1}{2}}}. \quad (2.5)$$

In million electron volts, we have

$$A^+ = -1.783 - \frac{78(I+1)}{A} + \frac{.58(A-I-1)}{A^{\frac{1}{2}}}. \quad \dots (2.6)$$

In the above derivations, we have taken β to be constant in the different groups. If we admit the possibility that

β may be a function of I , i.e. it changes from group to group, then we get

$$A^- = M_n - M_p - m + \frac{\beta(I)I^2 - \beta(I-2)(I-2)^2}{A} - \frac{\delta(A-I+1)}{A^{\frac{1}{2}}},$$

$$A^+ = -M_n + M_p - m + \frac{\beta(I)I^2 - \beta(I+2)(I+2)^2}{A} + \frac{\delta(A-I-1)}{A^{\frac{1}{2}}}. \quad \dots (2.7)$$

In this paper we shall, however, make no use of these formulae.

Lastly, we have

$$E^K = E^+ + m\{1 + (1 - \alpha^2 Z^2)^{\frac{1}{2}}\}, \quad \dots (2.8)$$

$$\simeq E^+ + 2m - \frac{1}{2}m\alpha^2 Z^2.$$

According to formulae (2.1) and (2.4), the values of E^+ and E^- depend on I , A , and the spin-dependent terms denoted by χ . It is therefore best to classify the nuclei into groups defined by definite values of the isotopic number I as Saha *et al.* (1940) have already done. We have, in the following, considered only a few groups at the beginning of the chart ranging from $I = -1$ to $I = 6$. For each group, we have drawn the A^+ and A^- curves, with the values of A^+ and A^- defined by (2.3) and (2.6) as ordinate and A as abscissa.

The groups with $I = \text{even}$, may be divided into two classes.

1. Even-even nuclei ($Z = \text{even}$, $N = \text{even}$): For such nuclei we have

$$\begin{aligned} E^- &= A^- + \chi(Z+1, A) < A^-, \\ E^+ &= A^+ + \chi(Z-1, A) < A^+, \end{aligned} \quad \dots (2.9)$$

because as has already been pointed out by Bohr and Wheeler (1939), $\chi(Z, A)$ is generally negative when Z is odd.

2. Odd-odd nuclei ($Z = \text{odd}$, $N = \text{odd}$): For these we have

$$\begin{aligned} E^- &= A^- - \chi(Z, A) > A^-, \\ E^+ &= A^+ - \chi(Z, A) > A^+, \end{aligned} \quad \dots (2.10)$$

because Z being odd, $\chi(Z, A)$ is negative.

When $I = \text{odd}$, we have to use the original formulae (2.1) and (2.4) as none of the χ -functions vanish. As we shall see later $\chi(Z \mp 1, A)$ and $\chi(Z, A)$ for odd-even or even-odd nuclei are in general nearly of the same order of magnitude so that $E^+ \simeq A^+$, $E^- \simeq A^-$ or may differ by only few units.

It is obvious that a nucleus is stable with respect to β^- -emission, when E^- is negative, and with respect to β^+ -emission when E^+ is negative. But K -capture can take place even if E^+ is negative but $> -2m$. The ratio between the frequencies of these two processes, in the case of allowed transitions may be estimated as follows. They are expressed

by the two factors f^K and f^+ where (see Konopinski, *loc. cit.*, pages 241 and 224)

$$f^K = 2\pi(\alpha Z)^{2s+1} (2R)^{2s-2} \left[1 + \frac{s}{(2s!)^2} \right] (E^K)^2, \quad (2.11)$$

$$\text{and } f^+ = u_+(Z)(\bar{p})^{2s-2} [v(W_0) - w_+(Z)(W_0 - 1)^3], \quad (2.12)$$

where $s = \sqrt{1 - \alpha^2 Z^2}$, $W_0 - 1 = \text{end-energy of the } \beta^+ \text{-spectrum in } m_0 c^2 \text{ units}$. The definitions of the functions $u_+(Z)$, $v(W_0)$, $W_+(Z)$, $\bar{p}$ may be found in Nordheim and Yost (1937). Numerical values of these functions will be found in the review by Konopinski (1943). A formula similar to (2.12) holds for negatron-emission. For small Z

$$f^K \simeq 2\pi(\alpha Z)^3 (E^K)^2. \quad \dots (2.13)$$

Deduction of E^- , E^+ and E^K from experimental data.—Radioactive nuclei release their energy in the form of energies of electrons, positrons, neutrinos, and γ -rays. In cases where we can be sure that no γ -rays are emitted, it is an easy matter to determine E^+ and E^- . These are, on current theories, merely equivalent to the end-energies of the β -ray spectra emitted by the nuclei, and whenever these end-energies have been correctly determined (this is by no means always the case) we have correct values of E^+ and E^- . It is more difficult to calculate E^K . This in the case of simple allowed K -capture is merely equivalent to the energy carried always by the 'neutrino', which is, however, unobservable. E^K has therefore in such cases to be determined from the energetics of the reaction, but this is possible only in a few cases (e.g. see the determination of E^K by Haxby *et al.*, 1940). In some cases E^+ and E^- also may be obtained from the energetics of the reaction which produces the nucleus in question.

When γ -rays are emitted, the situation becomes extremely complex. A satisfactory scheme of nuclear levels has to be devised to fit in with experimental results. These cases have been dealt with in their proper places. In such cases the energy liberated E is the sum of the end-energies of the emitted β -particles and the energies of the γ -rays genetically connected to these β -particles.

Let us now take up the different groups one by one and see how the inclusion of the term $\chi(Z, A)$ in the mass-defect formula of Weizsäcker and Bethe serves to explain the empirical rules of stability mentioned above. We shall see that the discussion for the odd groups is entirely different from that for the even groups so that we shall have to treat them separately. We shall first take up the odd groups $I = -1$, $I = 1$, $I = 3$, and $I = 5$ in §3. In §4 the even groups $I = 0$, $I = 2$, $I = 4$ and $I = 6$ will be discussed. In the discussion of each group we give a table in which all available information about the members of this group have been included. The methods of productions have been clearly indicated. The reactions characterised by the corresponding target nuclei being underlined, have been actually tried and the



references will almost in all cases be found in Seaborg's Table (Seaborg, 1944). When the target nucleus is not underlined, the corresponding reaction has not yet been tried.

§3. THE ODD GROUPS

A. The Group $I = -1$. (Fig. 2, Table 1.)

This group ranges from He^3 to Sc^{41} , leaving aside the proton which also algebraically belongs to this group. The nuclei Li^5 , B^9 , K^{37} have not yet been prepared. As will be clear from the transmutation chart in Table 1, we may perhaps produce Ti^{43} by the $\text{Ca}^{40}(\alpha, n)$ -reaction. He^3 is stable; all the rest are unstable, being either positron-emitting or decaying by K -capture.

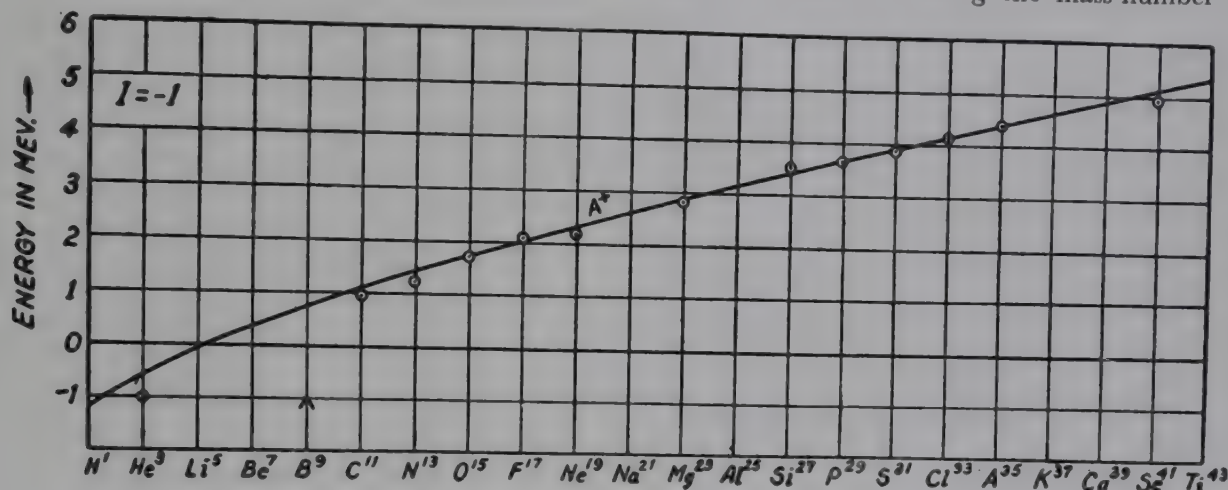


Fig. 2

It is easily seen that this group can have no β^- -activity, for A^- for this group is highly negative. The energy-release for positron-emission is given by the simple formula

$$E^+ = -1.788 + .58A^{\frac{2}{3}} + \chi(Z-1, A) - \chi(Z, A).$$

The formula for E^+ does not contain the mass-defect constant β . It may be noticed in passing that the expected theoretical energy-release from the nuclei of these groups has been expressed in a somewhat different formula by White *et al.* (1940). According to them

$$E^+ = -1.788 + \frac{.6(A-1)}{A^{\frac{1}{3}}},$$

They have assumed that the Coulomb energy term is given by

$$\frac{1.27Z(Z-1)}{A^{\frac{1}{3}}} \text{ mc}^2$$

(in electron-energy units) whereas we have followed Bethe who neglects 1 in comparison with Z and gets the usual expression

$$\frac{3}{5} \frac{Z^2}{r_0 A^{\frac{1}{3}}}$$

which in million volts is given by $.58 Z^2/A^{\frac{1}{3}}$.

The curve A^+ has been shown in Fig. 2. The points enclosed in small circles represent the experimentally observed values of E^+ . It will be noticed that the experimental points lie quite close to the A^+ -curve showing that $\chi(Z, A)$ and $\chi(Z-1, A)$ for these groups are nearly of the same magnitude. The β^+ -emission process for this group falls under the $0A$ class of Konopinski (1943). The difference of A^+ and the experimental value of E^+ gives us an estimate of $\chi(Z-1, A) - \chi(Z, A)$.

Let us now consider the nuclei one by one.

Li^5 : This nucleus is not yet known. It is theoretically very interesting because it formed the kernel of certain very remarkable astrophysical speculations. But neither Li^5 nor any other nucleus having the mass-number 5 has been

found so far. Since the abundance of Li^6 is only 7.5%, the $\text{Li}^6(n, 2n)$ -reaction would unambiguously be convenient if separated Li^6 could be available. The other two reactions are difficult to carry out on account of the fact that it is not easy to prepare a suitable target of He. The experiment may be tried, however, by bombarding solid or liquid helium with a proton or a deuteron beam. If Li^5 is found it will probably turn out to be either stable, or decaying by extremely slow K -capture process to He^5 , about which again there are very interesting speculations. We have shown later that if Li^5 is stable against break-up into He^4 , n it will decay by K -capture to He^5 in about five years' time.

Be^7 : According to investigations by Haxby *et al.* (1940) who studied Be^7 produced by the $\text{Li}^7(p, n)$ -reaction, the atomic mass-difference $\text{Be}^7 - \text{Li}^7$, in our notation $M(4, 7) - M(3, 7) = .87$ Mev. The nucleus shows K -capture as well as emission of a γ -ray of energy .450 Mev, the number of γ -rays to K -capture being 1:10 roughly. Attempt has been made by Breit and Knipp (1938) to explain the data on the basis that Li^7 has two nuclear states which can be designated as $P_{\frac{1}{2}}$, $P_{\frac{3}{2}}$; this is independently supported. Be^7 , which is supposed to have the state $P_{\frac{1}{2}}$, can have an

allowed K -capture producing Li^7 normal ($P_{\frac{3}{2}}$ -state) or a forbidden K -capture, producing Li^7 excited with $P_{\frac{1}{2}}$ -state. This excited Li^7 , while making a transition to normal $P_{\frac{3}{2}}$ -state, produces the γ -ray of energy $\cdot 450$ Mev. Breit *et al.* have given a theory of the phenomenon which has been revised by Konopinski. The $f_K t$ for Be^7 comes out to be ≈ 2300 , so that it supports the contention that the K -capture is allowed.

B^9 : This nucleus has not yet been found though the Be^9 (p, n)-reaction was studied by Haxby *et al.* (1940) and $M(5, 9) - M(4, 9)$ was given as $1\cdot08$ Mev, which would enable B^9 to emit positrons of energy $\cdot06$ Mev, or decay by K -capture to Be^9 . It is suggested by Bethe that B^9 , immediately on formation, breaks up into Be^8 , H^1 or into 2He^4 , H^1 , as the mass of B^9 is $\cdot20$ Mev higher than the $\text{Be}^8 + \text{H}^1$ -mass.

C^{11} : According to Haxby *et al.* (1940), the $M(6, 11) - M(5, 11)$ difference is $1\cdot97$ Mev corresponding to positron-emission of maximum energy $\cdot95$ Mev, which, as Haxby *et al.* remark, is in perfect agreement with the observed values of end-energy of β^+ -spectrum.

N^{13} : The emission of this nucleus has been studied by a large number of workers. We may refer to the work of Watase (1940). The nucleus emits also a weak γ -ray of energy $\cdot285$ Mev and a β -spectrum of complicated type.

are available about Na^{21} yet. The 7 sec. half-period assigned to Al^{25} by White *et al.* is not quite certain as yet. They have tried the reaction $\text{Mg} (p, n)$ so that they are not sure if the half-life observed is due to Al^{25} or Al^{26} . The β^+ -spectra of P^{29} , S^{31} , Cl^{33} , A^{35} have been studied in the cloud-chamber by White *et al.* (1941), who have given a theoretical discussion of this group. The figure for the last nucleus of this group Sc^{41} has been given by Elliot and King (1941). Though the spectra of all these nuclei, with the exception of that of N^{13} , appear to be of a simple type, detailed and accurate investigations about the form of the spectra are still lacking.

B. The Group $I=1$. (Fig. 3, Table 2.)

The group extends from H^3 to Ni^{57} . The methods of production are reviewed in Table 2. It appears possible from Table 2 to produce nuclei of this group beyond Ni^{57} , viz. Cu^{59} and Zn^{61} . We first review the known properties of these nuclei. The only β^- -emitting nucleus in this group is H^3 , for, as will subsequently be shown, He^5 if ever discovered will perhaps be stable. The stable nuclei extend in unbroken sequence from Li^7 to K^{39} , with the exception of A^{37} . This is a mild violation of Rule 2 of Saha *et al.* From Ca^{41} all are either β^+ -emitting or K -active. Let us consider the unstable nuclei in greater detail.

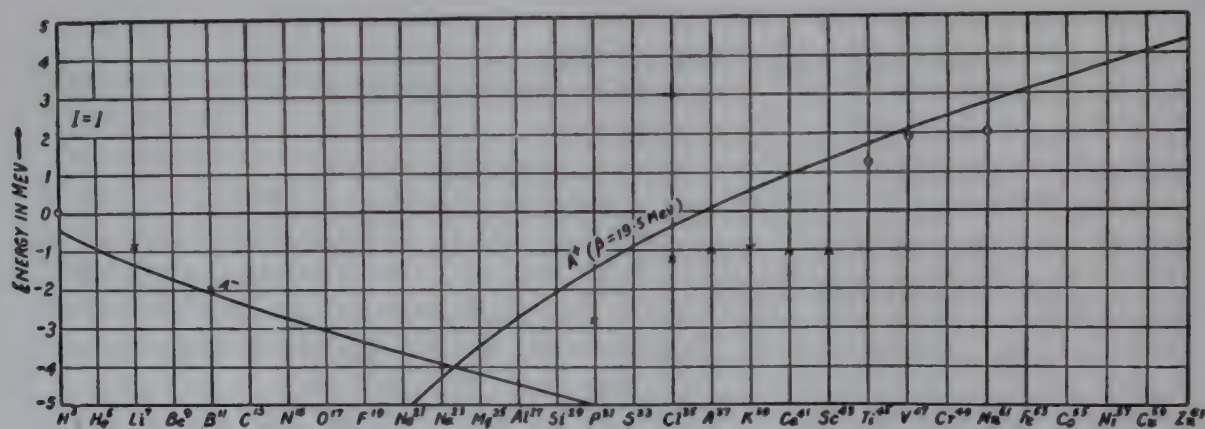


Fig. 3

Watase has given us an energy-level diagram from which it appears that the energy-release is $1\cdot21$ Mev, and the transition from the initial state of N^{13} to the final state of C^{13} is allowed. This is in accordance with the findings of Haxby *et al.* (1940). The γ -ray is from an excited state of C^{13} . It may be mentioned that the findings of Watase are in contradiction to those of previous workers, reference to whose works would be found in Watase's paper. These contradictions, however, refer to the γ -emission, not the value of the energy-release.

The value for end-energies of the β^+ -spectra for the nuclei O^{15} , F^{17} , Ne^{19} and Mg^{23} have been obtained by the cloud-chamber method and ought to be revised. No data

A^{37} : All that is known about this nucleus is from a brief note by Weimer *et al.* (1941) who state that it decays, presumably to Cl^{37} , with a long period of 34 days. Probably it decays by K -capture, but nothing is yet reported about the emissions.

Ca^{41} : This has been shown by Walke *et al.* (1940) to decay by K -capture to K^{41} with a life of $8\cdot5$ days. A γ -ray of energy $1\cdot1$ Mev, which is internally converted to an extent of 10^{-1} , is also emitted. The large conversion shows that spin-change in the transition is probably high. No positrons are yet recorded, though the γ -ray energy value indicates that positrons of low energy should be emitted.

Sc^{43} : This nucleus has been studied by Hibdon, Pool and

Kurbatov (1945) who found that it decays with a half-life of 3.92 hrs. to Ca^{43} by positron-emission, the end-energy being given as 1.11 Mev. It also decays by K -capture and a γ -ray of energy 1.65 Mev is emitted. The probability of positron-emission to K -capture is stated to be 4 : 1. The transition is of the $0B$ -type.

Ti^{45} : This nucleus has been prepared by Allen *et al.* (1941), by the process $\text{Sc}^{45} (p, n)$ and its spectrum has been found to have the end-energy of 1.2 Mev, with a life of 3.08 hrs., the transition being of the $0B$ -type. No γ -rays have yet been detected.

V^{47} : A 33-minute activity of radioactive vanadium has been ascribed to V^{47} by O'Connor *et al.* (1941) and the end-energy of the β^+ -spectrum has been found to be 1.90 Mev. The transition is of the $0B$ -type.

Cr^{49} : A 41.9 min. activity of radioactive chromium has been ascribed to Cr^{49} by O'Connor *et al.* (1941). The β^+ -spectrum was found to have the end energy 1.45 Mev, but a number of γ -rays with energies .18 Mev and 1.55 Mev have also been found. Cr^{49} decays to V^{49} which is radioactive and decays by K -capture to Ti^{49} . This sort of two-stage β^+ -emission happens in the case of every other subsequent nuclei of this class.

Mn^{51} : According to a preliminary report by Livingood and Seaborg (1938), this nucleus emits a simple β^+ -spectrum of end-energy 2 Mev (absorption). No γ -rays are reported. The transition is of the $0B$ -type. They did not observe the product Cr^{51} to decay. This was probably due to the fact that Cr^{51} (see $I=3$) decays mainly by K -capture, and emits no positron of measurable energy. The energy-release is of simple type and may be taken to be ≈ 2 Mev. The nucleus merits reinvestigation.

Fe^{53} : An 8.9 min. nucleus obtained by the process $\text{Cr}^{50} (\alpha, n)$ has been ascribed by Ridenour and Henderson (1937) to Fe^{53} and supported by others. The life is in agreement with expectations but nothing is yet known of β -emission.

Co^{55} : The identification of this nucleus which has been produced only by the processes $\text{Fe}^{54} (d, n)$ and $\text{Fe}^{54} (p, \gamma)$ would be considered doubtful, as Fe^{54} has a small percentage. It does not appear possible to prepare it with any other starting material, hence confirmation has to be sought by increasing the concentration of Fe^{54} . The identification has, however, been confirmed by Livingood and Seaborg (1941) from the observation that Fe^{55} with a long life of 5.3 yrs. grows from this nucleus, but the nature of emission from Co^{55} is more complex than that from any other nucleus of this group. The positron-spectrum was found to be complex by Lawson (1939) with end-energy at 1.50 Mev, but the observations were not refined enough for splitting the curve into its constituents. A number of γ -rays have been obtained in the cloud-chamber by Curtis (1939) giving lines at .16 Mev, .21 Mev, .8 Mev and 1.2 Mev, with intensities .1, .1, .5 and .1 of the annihilation radiation.

The complexity of emission from Co^{55} renders it difficult to make any deduction about its energy-release in the transition from $\text{Co}^{55} \rightarrow \text{Fe}^{55}$. The problem merits more detailed investigation.

Ni^{67} : Radioactive nickel, produced by the processes indicated in Table 2, does not allow a clear assignment of mass, vide the discussion on Ni^{59} in the group $I=3$. We have assigned the 2 min.-period nickel to Ni^{67} , in accordance with the views of several workers, but in opposition to the views of Nelson *et al.* (1941), where previous references and a discussion of the problem will be found. Nothing appears yet to be known about the emission from Ni^{67} , but the best way for the identification of Ni^{67} would be to see if Co^{67} of 270 days' life grows from it.

Cu^{69} : An 81 sec. copper obtained by Delsasso *et al.* (1939) from the process $\text{Ni} (p, n)$ has been assigned by the authors to Cu^{69} , but the assignment lacks confirmation. It would be interesting to observe the growth of Ni^{69} from the 81 sec. copper. Nothing as yet is known of its β^+ -emission.

Zn^{61} : It is not yet known. There is a possibility that it can be prepared by the process $\text{Ni}^{58} (\alpha, n)$. It does not appear probable to prepare any heavier nuclei of this group by an ordinary reaction.

Let us now compare the positron-emitters of the group $I=-1$ with the electron-emitters of the group $I=+1$. For the positron-emission of a nucleus ${}_Z M^A$ of any particular group I , we have

$$E^+(Z, A) = A^+(Z, A) + \chi(Z-1, A) - \chi(Z, A), \quad (3.1)$$

whereas for electron-emission of the nucleus ${}_{Z-1} M^A$ of the group $I+2$, we have

$$E^-(Z-1, A) = A^-(Z-1, A) + \chi(Z, A) - \chi(Z-1, A), \quad \dots (3.2)$$

so that

$$E^+(Z, A) + E^-(Z-1, A) = A^+(Z, A) + A^-(Z-1, A), \\ = -2m. \quad \dots (3.3)$$

It is easily seen that the right-hand side is independent of β . It is only necessary that β should be the same for the groups I and $I+2$. Thus taking the nuclei He^3 and H^3 , we get

$$E^+(2, 3) = -1.038 \text{ Mev} < -2m,$$

provided we take $E^-(1, 3) = .015$ Mev as given by Nielson (1941). Thus He^3 is definitely stable against K -capture decay as well as β^+ -decay. It is difficult to compare the energy-release of Li^5 with that of He^5 , for nothing definite is known about He^5 . We may, however, make a rough estimate of the E^- corresponding to He^5 and E^+ for Li^5 . Before doing this let us compare the energy-releases of Be^7 and Li^7 . As mentioned earlier Haxby *et al.* (1940) give

$$E^+(4, 7) = -.153 \text{ Mev},$$

so that from (3.3)

$$E^-(3, 7) = -0.87 \text{ Mev.}$$

Thus Li^7 should be stable against electron-emission as is actually the case. From (3.1) we get

$$\chi(4, 7) - \chi(3, 7) = 4.88 \text{ Mev,}$$

whereas from (3.2) we get

$$\chi(2, 3) - \chi(1, 3) = 4.57 \text{ Mev.}$$

This suggests that $\chi(3, 5) - \chi(2, 5)$ may be of the same order of magnitude so that setting it equal to the mean of the above two values we get from (3.2)

$$E^-(2, 5) = -0.462 \text{ Mev,}$$

so that He^5 should be definitely stable against β^- -emission. On the other hand from (3.1) we get

$$E^+(3, 5) = -0.561 \text{ Mev,}$$

for the heavier members of these two groups and it will be found that the fact that the remaining nuclei of the group $I=1$ are not β^- -active is consistent with the property that the corresponding nuclei of the group $I=-1$ decay by β^+ -emission or K -capture.

C. The Group $I=3$. (Fig. 4, Table 3.)

This group extends from O^{19} to Ga^{65} of which the nuclei from O^{19} to S^{35} are β^- -emitting. From Cl^{37} to Ti^{47} all are stable with the exception of A^{39} , a β^- -emitting nucleus. From V^{49} to Ga^{65} we have nuclei decaying by K -capture or positron-emission. A glance at the transmutation table (Table 3) will show that it is possible to extend this group on the lighter side to He^7 by the $\text{Li}^7 (n, p)$ -reaction. On the heavier side we may extend the group up to Ge^{67} by the $\text{Zn}^{64}(\alpha, n)$ -reaction.

Let us now examine the members one by one in detail.

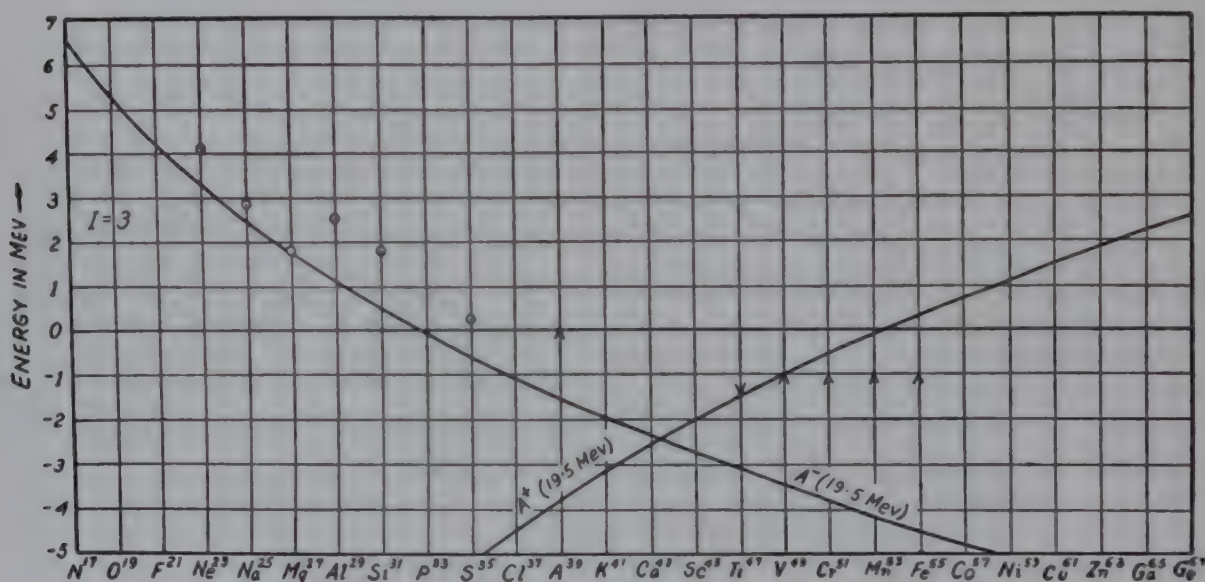


Fig. 4

so that Li^5 should be stable against β^+ -activity but should decay by K -capture. From equation (2.13), we get

$$f^k(3, 7) \simeq 1.37 \times 10^{-5}.$$

If K -capture decay for Li^5 is allowed, we may take $f^k t$ for this nucleus to be of the same order of magnitude as that for Be^9 , viz. 2300, so that for Li^5 the period of decay is expected to be

$$t(3, 5) \simeq 5 \text{ years.}$$

Next we may compare the energy-releases of B^9 and Be^9 . Since Be^9 is stable we may take $E^-(4, 9) < 0$, i.e. from (3.3) we get

$$E^+(5, 9) > -1.022 \text{ Mev.}$$

Thus the nucleus B^9 may be expected to decay by K -capture or β^+ -emission. In this way the discussion may be continued

O^{19} : Nothing is known of this nucleus, beyond a mere statement that it has a life of 31 sec. and that $E^- > 3.2$ Mev (Huber *et al.*, 1944). Probable methods of production are given in Table 3.

Ne^{23} : Huber *et al.* (1943) have produced the nucleus by the reaction $\text{Mg}^{26} (n, \alpha)$ and give a life of 40 sec., with $E^- = 4.1$ Mev.

Na^{25} : This has been investigated by Huber *et al.* (1943) who get a life of 62 sec. and $E^- = 2.8$ Mev.

Mg^{27} : The β^- -spectrum was investigated by the cloud-chamber method (Crittenden, 1939) and found to be 1.8 Mev. Other values are 2.05 Mev (Henderson, 1935) by absorption experiments and 1.96 Mev (Widdowson and Champion, 1938). No γ -rays are yet reported.

Al^{29} : As the end-energy of the β^- -spectrum has been obtained (Bethe and Henderson, 1939) by the cloud-chamber

only, the problem needs reinvestigation. The transition being of the 1A-type, there might be undetected γ -rays.

S^{31} : The end-energy of the β -spectrum has been obtained by the cloud-chamber (Kurie *et al.*, 1936) to be 1.08 Mev, and no γ -rays have been recorded. Evidently it needs reinvestigation.

S^{35} : Kamen (1941) gives end-energy of the β -spectrum as .120 Mev and A. K. Saha (1946) as .103 Mev. The f - t -value given by the latter is 2.37×10^4 and the transition is of 0B-class. Giebert *et al.* (1944) have studied the energetics of the reaction $Cl^{35}(n, p)S^{35}$, and find that there should be a γ -ray of energy .130 Mev, which is emitted in cascade, but is difficult to detect on account of its feeble intensity. The energy-release may be taken to be .233 Mev.

We now turn to positron-emitting and K -capturing nuclei.

V^{49} : A number of radioactive vanadium nuclei has been prepared by reactions with Ti, but as Ti has as many as 5 isotopes, it has been found difficult to assign the mass-number of the products correctly. According to Turner (1940) only V^{48} is unambiguously assigned. A 600-day vanadium has been assigned to be V^{49} by Turner after a good deal of argument. It has been found to emit neither β^+ nor γ -rays, but decays only by K -capture. This shows that $M(23, 49)$ has almost the same values as $M(22, 49)$. On the supposition that the energy of the neutrino released on K -capture is $x.mc^2$, where $x \ll 1$, we can calculate f^K . We have

$$f^K = 2\pi(\alpha Z)^3.x^2,$$

so that $f^K t = 1.56.10^6.x^2$. If the K -capture process of V^{49} is supposed to be of the allowed type then its $f^K t$ should be of the order 10^4 , i.e. we must have $x \simeq .1$.

Cr^{51} : Walke *et al.* (1940) have shown that Cr^{51} mainly decays by K -capture but positron-emission is also indicated by the emission of strong annihilation γ -rays of .5 Mev and 1.01 Mev. But no positrons were detected in the cloud-chamber. Recently Bradt *et al.* (1944) have given some new data about Cr^{51} . It gives vanadium K -rays indicative of K -capture, and a γ -ray of energy .330 Mev, which is converted to the extent of 2-3% in the K and L -levels, which indicate, using Dancoff's formula, that $\Delta i = 2$. It is estimated that only 3% of the transformations lead to the excited level of V^{51} which gives us the γ -ray. These authors contradict the report by Walke *et al.* that there is any γ -ray of energy $\simeq 1$ Mev. From these data, it is difficult to deduce any value for E^+ . It appears to be a small quantity.

Mn^{53} : This nucleus is not yet known. The probable methods of production are reviewed in Table 3. It should be easy to get this nucleus.

Fe^{55} : All that is known about this nucleus is from a short note by Livingood and Seaborg (1939) who state that according to private communication from Van Voorhis,

it has a long life of 4 yrs. It is stated to decay by K -capture mainly.

Co^{57} : A radioactive cobalt due to the reactions $Fe^{56}(d, n)$ and $Fe^{56}(p, \gamma)$ has been assigned to be Co^{57} by Livingood and Seaborg (1941). It emits β^+ -rays of end-energy .26 Mev and γ -rays of energies .117 Mev, .130 Mev, .202 Mev, and .215 Mev, whose internal conversions have been studied by Plesset (1941). It apparently decays by K -capture, but more extended investigations are necessary to disentangle the results.

Ni^{59} : On account of the methods of production of radioactive Ni-nuclei, it has been found difficult to assign the mass-number correctly. The 36 hrs.-half-life has been assigned to Ni^{57} by Livingood and Seaborg (1938) but to Ni^{59} by Doran and Henderson (1941). The latter assignment is more in agreement with our views and is adopted here. Ni^{59} does not appear to have been yet well investigated, but it is said to decay with the emission of a positron-spectrum of end-energy .67 Mev (absorption). According to Konopinski (1943) the transition is of 0B-type, with $ft = 6.5.10^4$, so that the energy-release in the transition $Ni^{59} \rightarrow Co^{59}$ can be taken to be .67 Mev. This nucleus should also decay by K -capture, but no observation appears to have been made so far.

Cu^{61} : This nucleus has been found to decay both by positron-emission and K -capture (Alvarez, 1938). The end-energy of the β^+ -spectrum of Cu^{61} was given by Ridenour and Henderson (1937) at .94 Mev, but the spectrum has been reinvestigated by Bradt *et al.* (1945) who find $E^- = 1.225$ Mev. Calculation with this value shows $f^K/f^+ \simeq .278$ and the ratio of the number of Ni K -quanta to the number of annihilation quanta was found to be .33.

Zn^{63} : Townsend (1941) found the positron-spectrum end-point at 2.30 Mev and a γ -ray of energy 1.50 Mev was also suspected. According to our calculation $f^+/f^K \simeq 20$ so that K -capture is expected to be very feeble. In fact it is not reported at all. $ft \simeq 1.55.10^5$ and the transition is assigned to the 0B-class, but it is really midway between 0B and 1B. The energy-release may be taken to be 2.30 Mev.

Ga^{65} : A 15-minute gallium produced by the processes $Zn(d, n)$ and $Zn(p, \gamma)$ has been provisionally assigned to be Ga^{65} , but the investigations are rather preliminary.

We may now compare the positron-emitters of the group $I=1$ with the electron-emitters of the group $I=3$. To compare P^{31} with Si^{31} we put $E^-(14, 31) = 1.8$ Mev in (3.3) and get thereby

$$E^+(15, 31) = -1.359 \text{ Mev} < -2m.$$

Thus P^{31} is stable against β^+ -decay as well as K -capture as is actually observed. Next we take the isobaric pair S^{33} and

P^{33} . Since S^{33} is stable we may put $E^+(16, 33) < -1.022$ Mev, and consequently from (3.3)

$$E^-(15, 33) > -.003 \text{ Mev.}$$

Thus we cannot definitely say whether P^{33} , if ever prepared, will show β^- -activity or be stable against it. But it is very likely that this nucleus would be β^- -active decaying to S^{33} . Next pair is Cl^{35} and S^{35} . If $E^-(16, 35)$ is taken to be .233 Mev, then from (3.3)

$$E^+(17, 35) = -1.257 \text{ Mev} < -2m,$$

so that Cl^{35} should be stable as actually observed. We may now try to explain the anomalous behaviour of A^{37} . To do

D. The Group $I=5$. (Fig. 5, Table 4.)

This group extends from S^{37} to Ge^{69} . We have five β^- -emitting nuclei from S^{37} to Sc^{47} . From Ti^{49} to Cu^{63} , we have eight stable nuclei, followed by two K -active and positron-emitting nuclei. The methods of production of the radioactive nuclei are reviewed in Table 4. It appears possible to extend the group on both flanks. Attempts may be made to produce Cl^{39} by the $S^{36}(\alpha, p)$ -reaction. S^{36} (frequency .016%) has to be concentrated. Beyond S^{37} , it appears possible to go up to Si^{33} . On the other flank, it will be possible to go up to Sr^{81} .

Let us review the β^- -emitting nuclei one by one.

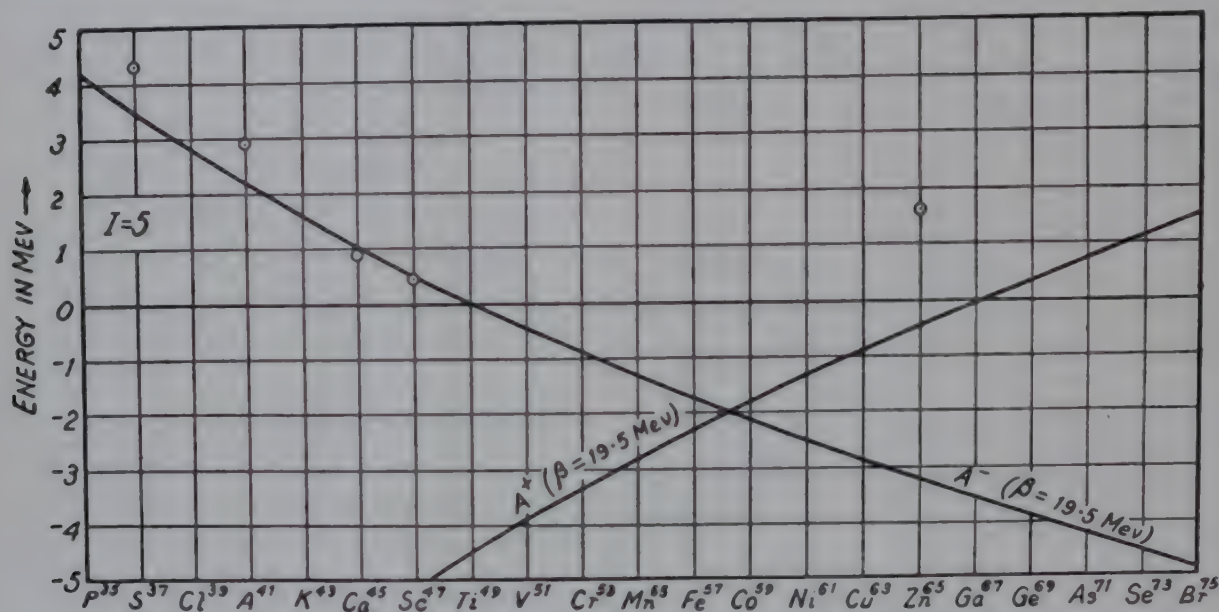


Fig. 5

this we put $E^-(17, 37) < 0$, as Cl^{37} is stable. Thus from (3.3) we have

$$E^+(18, 37) > -1.023 \text{ Mev} \approx 2m.$$

Thus A^{37} should show β^+ -emission or K -capture, and this is in concord with experimental facts. We can estimate $E^K(18, 37)$ on the hypothesis that the K -capture of A^{37} is allowed. If $f^K t$ is taken to be of the order 3450 (the value for Sc^{41}) then we have $E^K(18, 37) \approx .15$ Mev and consequently $E^+(18, 37) \approx -.87$ Mev showing that A^{37} will most probably not show β^+ -decay. We may next explain the anomalous behaviour of A^{39} by comparing this nucleus with K^{39} . As K^{39} is stable against β^+ -decay as well as K -capture, we have $E^+(19, 39) < -1.022$ Mev so that from (3.3)

$$E^-(18, 39) > 0,$$

showing that A^{39} should show β^- -activity, which fact is in harmony with the finding that there is no stable isotope of A having the mass-number 39. In this way we may continue our discussion for the heavier members of the two groups.

S^{37} : It has been identified by Giebert *et al.* (1944) in a $Cl+n$ -reaction with a 5 min. product. It shows a complex β^- -spectrum, 10% decaying with the end-energy 4.3 Mev, 90% with the energy 1.6 Mev, and a strong γ -ray of energy 2.8 Mev has been found. Apparently, the end-energy is 4.3 Mev.

A^{41} : According to a rather old investigation by Richardson and Kurie (1936) with the cloud-chamber, this nucleus emits a β^- -spectrum with the end-energy of 1.5 Mev and a γ -ray of energy 1.37 Mev. The genetic connection has not yet been investigated. The β -transition has been found to be of the $1A$ -type as $ft = 2.7.10^5$. If the two rays follow in succession, $E^- = 2.87$ Mev.

K^{43} : Nothing is known about this nucleus.

Ca^{45} : This emits a composite β^- -spectrum of end-energies .19 Mev (95%) and .91 Mev (5%) and a γ -ray of .71 Mev. Evidently the energy-release is .91 Mev.

Sc^{47} : Hibdon and Pool (1945) have given reasons for assigning the 63 hrs. radioactive scandium to Sc^{47} . The end-energy according to them is at .46 Mev. There are

apparently no γ -rays. $ft \approx 1.6 \cdot 10^5$, so that the class is 0B. Energy-release may be taken to be .46 Mev.

We now turn to the positron-emitting and K -capturing nuclei.

Zn^{65} : This nucleus has been investigated by a large number of workers, but we may take only the work of Watase *et al.* (1940). They found that it emits a positron-spectrum ending at .46 Mev and a number of γ -rays at

§ 4. THE EVEN GROUPS.

A. The Group $I=0$. (Fig. 6, Table 5.)

This group extends from He^2 to Cu^{58} , the last nucleus being rather doubtful. Be^8 does not occur in nature and probably breaks up into two α -particles (He^4) as soon as it is formed, and nuclei from Ti^{44} to Ni^{58} have neither been found in nature nor have been artificially produced.

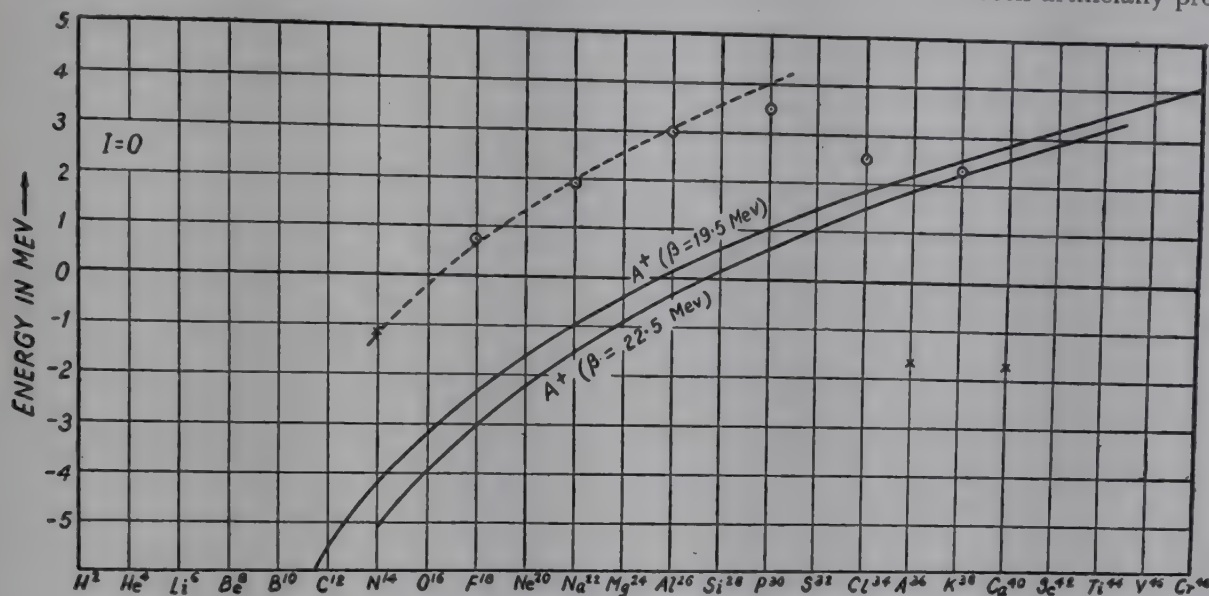


Fig. 6

.45 Mev, .65 Mev and 1.0 Mev. They have established that Zn^{65} decays mainly by K -capture, because the nucleus emits the K -line of Cu^{65} . The γ -lines are evidently due to excited Cu^{65} , produced by K -capture. The ratio of K -capture to positron-emission is given as 70 : 1. The total energy-release is given by these authors as either 1.4 Mev or 1.6 Mev.

Ga^{67} : Though this nucleus has been studied by numerous investigators, its spectrum has not yet been cleared up. It emits a number of γ -rays whose energies are given by Cork *et al.* (1942) as .094 Mev, .174 Mev, .187 Mev and .301 Mev, and other workers give nearabout figures. Of these .094 Mev γ -ray is the most heavily converted. The nucleus is presumed to decay by K -capture but from the present data, it does not appear possible to obtain any idea of the energy-release in the transition Ga^{67} to Zn^{67} .

Ge^{69} : Nothing is known about this nucleus beyond the mere statement that it has a long life of ≈ 195 days. The report appears to be extremely doubtful.

The comparison between the positron-emitting nuclei of the group $I=3$ with the electron-emitting nuclei of the group $I=5$ may be done in the same manner as has been shown for the other groups.

Four exceptions to the empirical rules of stability are found in this group. These are shown with their spins and magnetic moments in Table 5a. These nuclei in spite of

having both N and Z odd are not unstable. But the other odd-odd nuclei of the group follow Rule I, i.e. all the

TABLE 5a.

	H^1	Li^6	B^{10}	N^{14}	F^{18} (β^+ -active).
Spin i	1	1	1	1	1?
Magnetic moment	.8565	.8213	.598	.403	

known odd-odd nuclei from F^{18} onwards are all β^+ -active. All the even-even nuclei of this group are stable as required by Rule I. The facts find ready explanation on the theory proposed. The course of the A^+ -curve are shown in Fig. 6. The A^- -curve, not shown in the figure, is so far down in the negative energy domain that even for odd-odd nuclei, for which $E^- > A^-$, we cannot have E^- positive. This explains why we have no β^- -emitting nuclei in this group.

We have, as mentioned in §1, for even-even nuclei $E^+ < A^+$ and for odd-odd nuclei $E^+ > A^+$, where

$$A^+ = -1.788 - \frac{4\beta}{A} + \frac{\delta(A-1)}{A^{\frac{1}{2}}}$$

The stability of Li^6 , B^{10} , N^{14} is explained on the supposition that for these nuclei $A^+ - \chi(Z, A)$ continues to be negative because A^+ is negative and $|A^+| > -\chi(Z, A)$. Only from F^{18} onwards, $A^+ - \chi(Z, A)$ becomes positive.

Let us review the different members one by one.

F^{18} : It appears to show a simple β^+ -spectrum of the 0A-type, but more extended investigations are desirable. We have assumed that there are no γ -rays and $E^+=70$ Mev, as given by Yasaki and Watanabe (1938) in a short note. It is quite possible that F^{18} may also decay by K -capture to O^{18} , for according to calculation for allowed transition $f_K/f^+ \simeq \frac{1}{2}$.

Na^{22} : This emits both β^+ -rays of end-energy 58 Mev and a γ -ray of energy 1.3 Mev. According to an extensive investigation by Maier-Leibnitz (1944), there is one γ -ray per β -ray, hence the energy-release is in cascade and equals $58+1.30=1.88$ Mev. The β -transition therefore is to an excited state of Ne^{22} .

Al^{26} : This appears to emit, according to cloud-chamber investigations of White *et al.* (1939), a β^+ -spectrum with end-energy at 2.99 Mev, the transition being of the 0A-type. Hence we have to take the total energy-release to be 2.99 Mev.

P^{30} : This nucleus emits, according to Magnan (1941) a β^+ -spectrum with end-energy at 3.5 Mev, the transition being of the 1A-type. A γ -ray emission is therefore probable, though it has not yet been detected.

Cl^{34} : The end-value of the β^+ -spectrum (2.5 Mev) is available only from absorption experiments and requires revision. On the present data, the transition is of the 1A-type, so that a γ -ray is possible. The value of E^+ cannot therefore be found from present data.

K^{38} : This does not appear to be well-studied.

Sc^{42} : A radioactive scandium of 13.5 days period produced by the reaction $K^{39}(\alpha, n)$ was reported by Walke (1940), but this has not been confirmed by Hibdon, Pool

and Kurbatov (1945). It appears also unlikely that Sc^{42} can have such a long period as 13.5 days.

A smooth curve can be drawn through the E^+ -values of F^{18} , Na^{22} , Al^{26} and P^{30} and it is worthwhile investigating, when more complete data about Cl^{34} and K^{38} are obtained, whether this curve can be extended through their E^+ -points.

We have, as yet, no knowledge of any attempt to produce heavier nuclei of this group. But it appears possible to produce some heavier nuclei with odd Z , viz. V^{46} , Mn^{50} , Co^{54} and Cu^{58} by using the (p, n) -reactions. They are expected to decay by the emission of positrons of very high energy. Will it be possible to produce nuclei of even Z , heavier than Ca^{40} , e.g. Ti^{44} , Cr^{48} , etc.? We have not yet been able to think of any method. But if they can be produced, they will not be stable, for we have

$$\begin{aligned} E^+(20, 40) &= 2.90 + \chi(19, 40) \text{ Mev} \\ \text{whereas} \quad E^+(22, 44) &= 3.51 + \chi(21, 44) \text{ Mev.} \end{aligned}$$

Since Ca^{40} is stable, and does not decay by K -capture — $\chi(19, 40) < 2.9$ Mev and we can put also $-\chi(21, 44)$ to be of this order. Hence E^+ for $Ti^{44} \simeq -4$ Mev, i.e. Ti^{44} will probably decay by K -capture to Sc^{44} which will then decay by positron-emission to Ca^{44} . Other nuclei having $I=0$, beyond Ti^{44} , all nuclei would have E^+ -positive, even if N and Z are even. But while odd-odd nuclei are expected to emit positrons of great energies, the even-even ones will emit positrons of much smaller energies and the earlier ones in the even-even group will mostly decay by K -capture.

B. The Group $I=2$. (Fig. 7, Table 6.)

This group extends from the doubtful nucleus H^4 to Ga^{64} . Of this group, all odd-odd nuclei are unstable as

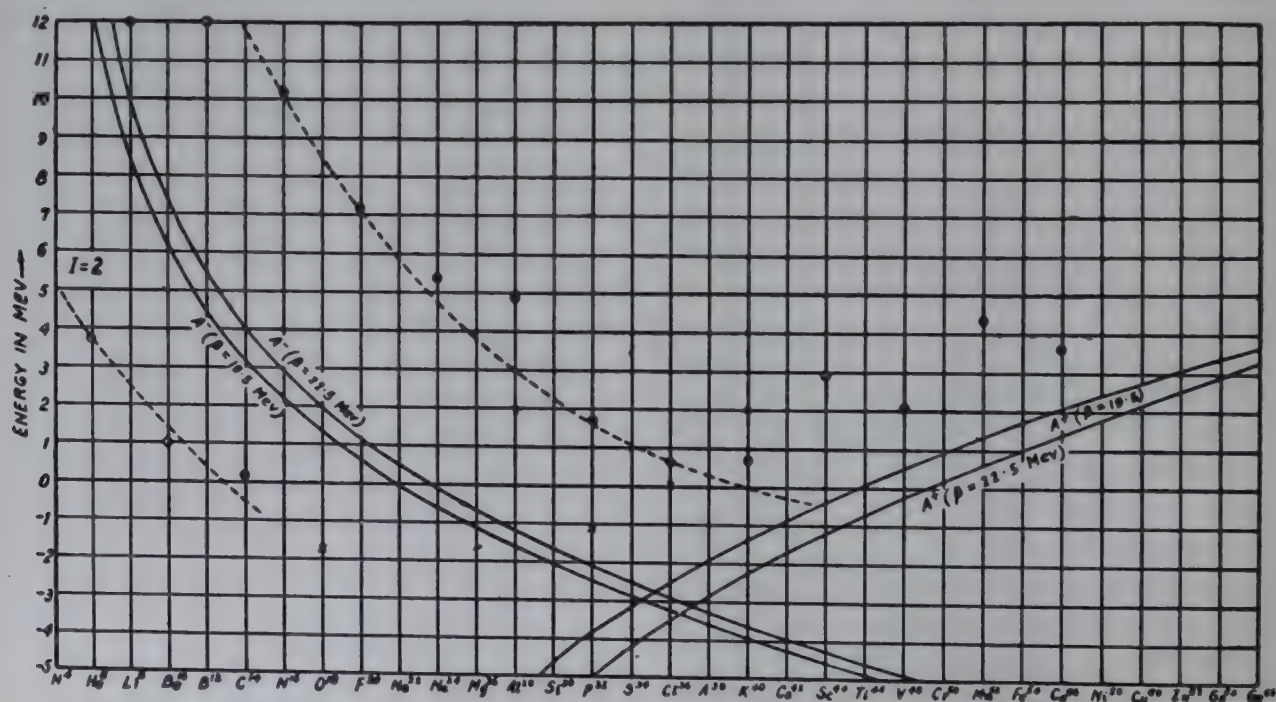
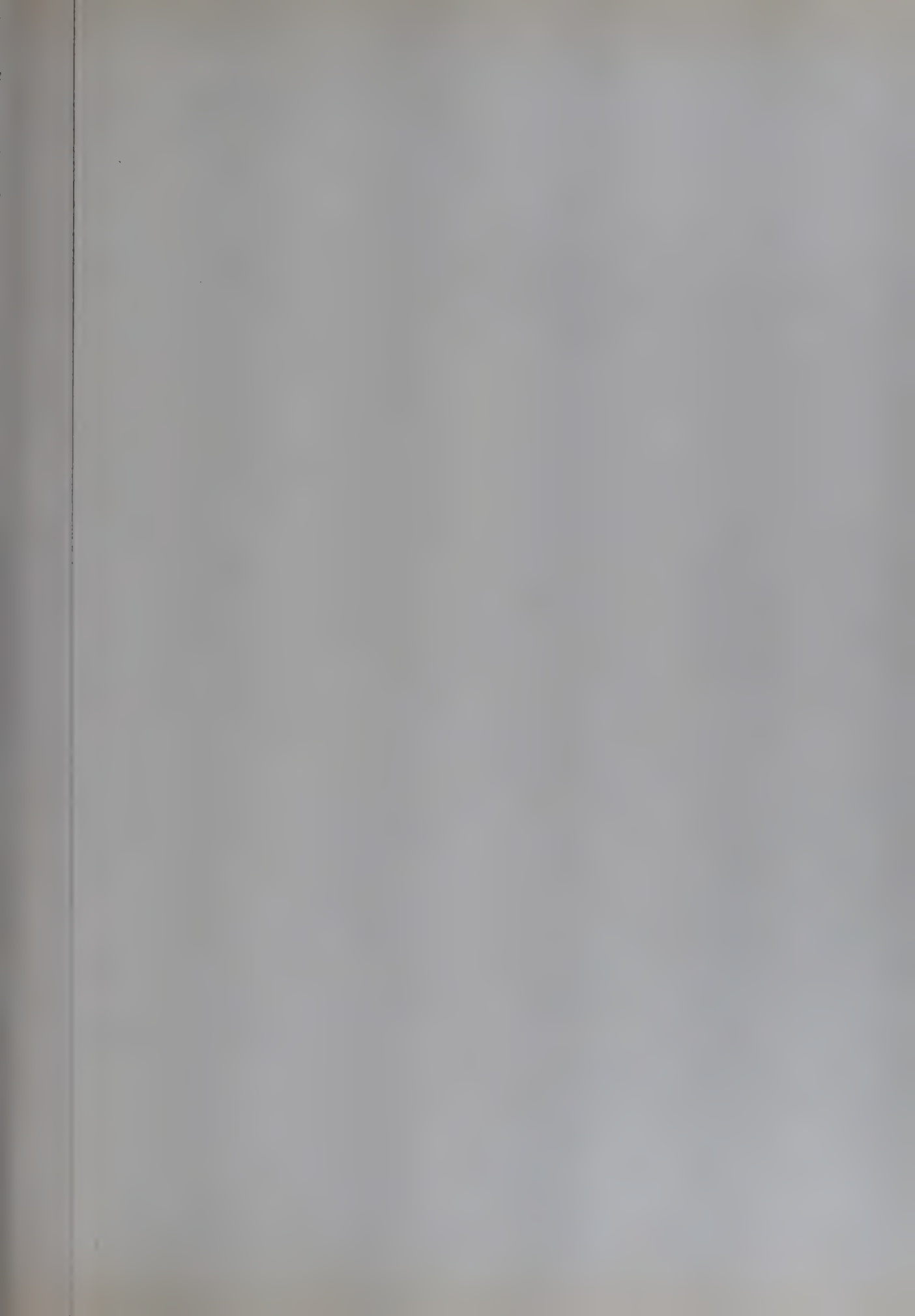


Fig. 7



stated in §1, but as already mentioned He^6 , Be^{10} , C^{14} are unstable, though both N and Z are even. But it may be noticed that the total energy-releases E^- for these even-even nuclei are much less than those of immediate neighbours with Z odd and N odd, e.g. E^- for Be^{10} is 1 Mev while that for B^{12} is 12 Mev. The general explanation of these facts may be obtained from formulae (2.9) and (2.10). It has been proved there that for the even-even nuclei of an even group, $E^- < A^-$ whereas for the odd-odd nuclei of the same group, $E^- > A^-$. A glance at Fig. 7 will show that such is indeed the case. In this figure, the $A^\pm$ -curves have been drawn for two values of β , viz. 19.5 Mev and 22.5 Mev. In both cases we find that points indicating E^- for the even-even nuclei He^6 , B^{10} , C^{14} lie below the $A^\pm$ -curve, whereas for the odd-odd nuclei Li^8 , B^{12} , N^{16} , F^{20} , etc. the points indicating E^- lie above the A^- -curve. In Table 6a, we have calculated A^- for the nuclei He^6 to F^{20} , taking $\beta=22.5$ Mev. Probably the formula is not applicable to the lightest elements, but that does not matter much. We observe that the spin-independent part is large to start with and diminishes gradually as A is increased, while $\chi(Z, N)$ remains almost of the same magnitude.

Be^{10} : All that is known about this nucleus is a private communication from Macmillan to Seaborg (1944). The nucleus requires reinvestigation. It is a long-lived product with life $\approx 10^3$ years, with a small end-energy because A^- and χ are now subtractive.

B^{12} : All the remarks made with respect to Li^8 apply to this nucleus.

C^{14} : The emission of this nucleus has been studied by Ruben and Kamen (1940) who conclude from absorption experiments that the value of the end-energy of the β^- -spectrum is 145 ± 0.15 Mev. They could detect no γ -rays. In view of the limitations of such extrapolation formula for such low energy β -rays it is desirable that the limit be redetermined with the screen-cathode β -ray spectrometer (Saha, 1944). The transition $\text{C}^{14} \rightarrow \text{N}^{14}$ appears to be highly forbidden, like that of Be^{10} , while that of He^6 is allowed. It is quite probable that there are undetected γ -rays from C^{14} though Ruben and Kamen could not detect any of greater energy than 0.1 Mev.

N^{16} : It has been recently investigated by Sommers Jr. and Scherr (1946) who find that the β^- -spectrum emitted by it is complex. The total energy-release appears to be $E^- = 10.2 \pm 0.5$ Mev. 25% of the disintegration consists of

TABLE 6a.

Nucleus	Odd-Odd								Even-Even		
	Li^8	B^{12}	N^{16}	F^{20}	Na^{24}	Al^{28}	P^{32}	Cl^{36}	He^6	Be^{10}	C^{14}
A^- in Mev	9.98	5.48	2.93	1.20	-1.1	-1.18	-2.09	-2.89	14.17	7.34	4.06
E^- in Mev	$12+x$	12	10.2	7.2	5.4	5.1	1.72	.64	3.5	1	.145
$-\chi(Z, A)$ in Mev	$2.02+x$	6.52	7.27	6	5.51	6.28	3.81	3.53	10.67	6.34	4.915
(Z, A)	(3, 8)	(5, 12)	(7, 16)	(9, 20)	(11, 24)	(13, 28)	(15, 32)	(17, 36)	(3, 6)	(5, 10)	(7, 14)

Let us consider the electron-emitters of this group one by one.

He^6 : This interesting nucleus, first reported by Bjerger and Broström (1936) has recently been studied by Sommers Jr. and Scherr (1946) who confirm the earlier findings that $E^- = 3.5 \pm 0.6$ Mev. The transition is allowed as $f \approx 1160$, according to Konopinski (1943).

Li^8 : The value of end-energy is very large because the A^- -term and χ -term are now additive. A reference to the original work by Bayley and Crane (1937) shows that the determination of the end-energy of the β^- -spectrum by cloud-chamber method carried out by them needs revision both for Li^8 and B^{12} . It is quite possible that in addition to β -rays, Li^8 may emit also γ -rays.

a direct transition from the initial level of N^{16} to the final level of O^{16} but for the remaining 75%, we have first a β^- -transition to an intermediate level of 4 Mev, which is followed by a γ -ray of energy 6.2 Mev.

F^{20} : This nucleus has been studied by Bower and Burcham (1940) who find that the end-energy of the β^- -spectrum is about 5 Mev, but this is followed by a γ -ray of energy 2.2 Mev. The total energy-release may therefore be taken to be 7.2 Mev, though more extended investigations are necessary to elucidate the problem.

Na^{24} : This very famous nucleus emits a β^- -spectrum and number of γ -rays, which have been the subject of numerous investigations. The latest are those by Krüger and Ogle (1945), and by Maier-Leibnitz (1944) who have given

level schemes. According to the latter, the total energy-release in the transition $\text{Na}^{21} \rightarrow \text{Mg}^{21}$ is 5.4 Mev whereas according to Krüger and Ogle it is 5.28 Mev. There is not much difference between these two values, and we have taken 5.4 Mev as the energy-release.

Al^{28} : Itoh (1941) has given a discussion of the β^- and γ -ray spectrum of this nucleus in a paper where all previous references would be found. The best value of the end-energy of the β^- -spectrum is 3.3 Mev and the γ -ray energy is 1.8 Mev. According to the β - γ coincidence experiments of Watase (1941), one γ -ray is emitted per β^- -transition, hence the energy-release is 5.1 Mev. Mass-data of Barkas as well as our investigations would, however, indicate that the energy-release is ≈ 3.2 Mev.

P^{32} : According to Lawson (1939), this nucleus has a simple β^- -ray spectrum with an end-point at 1.72 Mev. Searching investigations have failed to show any γ -ray. The spectrum certainly creates theoretical difficulties and has been the subject of numerous investigations.

Cl^{36} : All information about this nucleus are from a note by Grahame and Walke (1941), who say that the β^- -spectrum is simple with the end-point at .64 Mev. There are apparently no γ -rays. A few tracks apparently of low-energy positrons from the source were obtained in the cloud-chamber, as well as γ -rays which are supposed to indicate K -capture. A more detailed and accurate investigation of Cl^{36} is very much desirable for it apparently decays on one side by β^- -emission to A^{36} , and on the other side by K -capture and positron-emission to S^{36} . So Cl^{36} is the first nucleus which, like Cu^{64} , decays on two sides. As we shall see later, Cl^{36} is one of the key-nuclei which can give us very useful information.

K^{40} : This nucleus occurs in nature with a frequency of 1/8000, and accounts for the natural radioactivity of potassium, discovered since 1906. It may also be artificially produced, but none of the methods suggested in Table 6 has yet been tried. On account of the long life of this nucleus and its low abundance, it is difficult to make accurate measurements with K^{40} . A large quantity of material is required so that all measurements become inaccurate due to self-absorption. Hence, measurements given by different observers have been widely different, e.g. the end-value of β^- -spectrum is given as .725 Mev by Libby and Lee (1939) while Henderson (1938) gives 1.3 Mev. The nucleus decays by β^- -emission to Ca^{40} and Thomson and Holt (1944) have given arguments to show that it decays by K -capture to A^{40} , the proportion of the K -capture to β^- -emission being given as 4 : 1. As we shall see shortly, the possibility of positron-emission cannot be excluded. The spin of K^{40} has been directly measured and found to have the abnormally large value of 4 (Zacharias, 1941). This short review shows the extremely unsatisfactory nature of our knowledge of K^{40} and attempts may be made to produce this nucleus by artificial methods, e.g.

by the $\text{K}^{30} (d, p)$ -reaction, and see whether the properties of K^{40} so obtained are similar to those of K^{40} occurring in nature. Isomeric forms of K^{40} having shorter life are quite possible.

All the odd-odd nuclei after K^{40} decay definitely by K -capture and β^+ -emission. We may take them for detailed examinations.

Sc^{44} : A large amount of work has been done with this nucleus, but we may refer only to the recent work of Hibdon, Pool and Kurbatov (1945), for this work is quite elaborate and contains all references to earlier works. They have found that Sc^{44} , as derived from $\text{K}^{41} (\alpha, n)$ and $\text{Sc}^{45} (n, 2n)$ -reactions, consists of two isomers, having lives of 3.92 hrs. and 52 hrs. The 52 hrs. isomer decays into the 3.92 hrs. one by emitting a γ -ray of energy .28 Mev which is highly converted. The 3.92 period Sc^{44} emits a β^+ -spectrum of end-energy 1.33 Mev and a γ -ray of energy 1.35 Mev. K -capture decay for Sc^{44} is indicated but it has not been definitely proved by X-ray investigations. According to calculations we have for allowed transitions $f_K = .479, f^+ = .588$ so that $f_K/f^+ = .8$. The positron-emission is of the $1A$ -type, as $f^+t = 1.19 \times 10^5$. The number of γ -rays to β^+ -emission is given as 3 : 1, which does not agree with our ratio of f_K/f^+ showing that the process is more complicated. All that we can say from these investigations is that the energy-release is > 1.61 Mev.

V^{48} : According to the recent work of Hibdon *et al.* (1944), the end-energy of β^+ -emission is .58 Mev. The transition is of the $1B$ -type. There is only one γ -ray of energy 1.5 Mev. This is the only radioactive isotope of vanadium which according to Turner (1940) is unambiguously identified. V^{48} has been observed to decay by K -capture and the probability of K -capture decay to that of β^+ -emission has been found to be 18 : 1 (Hibdon *et al.*, 1944). It is found on our calculation that $f^+ = .154, f_K = .292$. The ratio of $f_K/f^+ = 2 : 1$, and not 18 : 1.

Mn^{52} : This nucleus has been investigated in detail by Hemmendinger (1940) and has been found to consist of two isomers having periods of 21 min. and 6.5 days. The 21 min.-isomer emits a positron spectrum of end-energy 2.2 Mev with a transition of the $0B$ -type and the 6.5 days-isomer, one of end-energy .77 Mev with a transition of the class $1B$. A number of γ -rays are emitted by each isomer and K -capture is also inferred. It does not, however, appear to us that the level scheme suggested by Hemmendinger (Hemmendinger, *loc. cit.*, Fig. 9, p. 934) is correct. The energy-release according to this scheme is 5.4 Mev which appears to be too high. Mn^{52} appears to be one of the most interesting nuclei for investigation, for it gives a lot of data not yet cleared up.

Co^{56} : This nucleus has been the subject of many investigations which have been summed up by Elliot and Deutsch (1943). They have also given a level scheme (Figure on p. 324 of their paper). According to this paper, the total

energy-release in the transition $\text{Co}^{56} \rightarrow \text{Fe}^{56}$ is 3.605 Mev, which occurs in the form of a β^+ -spectrum of end-energy 1.5 Mev, followed by two γ -rays in cascade, of energies 1.26 Mev and .845 Mev respectively. The last ray is found in the spectrum of Mn^{56} as well and must be from an excited state of Fe^{56} . Co^{56} also is suspected to decay by K -capture and the ratio of f_K/f^+ for allowed transitions = .25. On account of K -capture, a large number of γ -rays are emitted.

Cu^{60} and Ga^{61} have been claimed to have been produced by the processes $\text{Ni}^{60}(p, n)$ and $\text{Zn}^{61}(p, n)$ respectively, but nothing is known yet about their emissions. It does not appear possible to produce Zn^{62} , Ge^{66} , etc. which are not yet known amongst the stable nuclei of this group, artificially by any of the commoner nuclear processes. But unfamiliar processes like $\text{Ni}(\alpha, 2n)$, $\text{Cu}^{63}(p, 2n)$ may be thought of. But if these nuclei are formed, they will appear to be unstable (cf. discussion on Ti^{44} in the group $I=0$) and decay with β^+ -emission and K -capture to Cu^{62} and Ga^{66} respectively, which will again decay by β^+ -emission to Ni^{62} and Zn^{66} .

Discussion: It has been found difficult in this group to compare the theoretical formulae with the experimental results, because the latter are extremely confusing, and incapable of unique interpretation. For many nuclei, the knowledge is extremely defective. We shall show, however, that we may fix the value of the mass-defect constant β by a close analysis of the data collected for the nuclei P^{32} , Cl^{36} and K^{40} . It is clear that the value of β affects the two curves to different degrees and in opposite senses, e.g. for $I=2$ we have

$$A^- = .766 + \frac{4\beta}{A} - \frac{\delta(A-1)}{A^{\frac{1}{2}}}, \quad A^+ = -1.788 - \frac{12\beta}{A} + \frac{\delta(A-3)}{A^{\frac{1}{2}}},$$

so that any increase in the value of β will depress the A^+ -curve thrice as much as it elevates the A^- -curve. Now from equation (2.10) we have for odd-odd nuclei

$$\frac{E^-(Z, A) - E^+(Z, A)}{2} = \frac{A^-(Z, A) - A^+(Z, A)}{2} \\ = 1.227 + \frac{4\beta I}{A} - \frac{\delta(A-I)}{A^{\frac{1}{2}}}. \quad (4.1)$$

If $\beta = 19.5$ Mev, then for the nucleus P^{32} we have, since $E^-(15, 32) = 1.72$ Mev,

$$E^+(15, 32) = .379 \text{ Mev},$$

so that P^{32} ought to decay by K -capture and β^+ -decay, a fact which is not borne out by experimental observations. To make P^{32} stable against β^+ -emission and K -capture we take

$$E^+(15, 32) = -1.022 - y \text{ Mev},$$

where $y > 0$. From equation (4.1) we get

$$\beta = 22.118 + 2y \text{ Mev}.$$

In Fig. 7 we have drawn the $A^\pm$ -curves for $\beta = 22.5$ Mev. Let us now see whether the fact that Cl^{36} exhibits double activity is consistent with this new value of β . Using equation (4.1) we have, taking $E^-(17, 36) = .64$ Mev,

$$E^+(17, 36) = .034 \text{ Mev} > 0,$$

i.e. Cl^{36} ought to decay by both β^+ -decay as well as by K -capture as is actually observed. For K^{40} we do not have any exact evaluation of $E^-(19, 40)$; but if we take it to be .7 Mev, we get

$$E^+(19, 40) = 2.04 \text{ Mev},$$

so that K^{40} ought to decay not only by K -capture but also by β^+ -emission. The difficulties about the measurements for K^{40} have already been mentioned. It is quite possible that this energy $E^+(19, 40)$ may be released in the form of positrons and γ -rays. This deduction is supported by Klemperer (1934) who gives two γ -rays of energies .5 Mev and 2 Mev. The former appears to be annihilation radiation, which is a strong proof that K^{40} actually decays by β^+ -emission. K^{40} is thus seen to be full of unsolved problems, though it was the oldest light radioactive element discovered.

We may now compare the isobaric pairs of the groups $I=0$ and $I=2$. To do this we have drawn in Fig. 6 the A^+ -curve for $I=0$ corresponding to $\beta = 22.5$ Mev. First we have the isobaric pairs N^{14} and C^{14} . Since $E^-(6, 14) = .145$ Mev we get using (3.3)

$$E^+(7, 14) = -1.169 \text{ Mev} < -2m.$$

Thus N^{14} should be stable against β^+ -emission or K -capture as is observed. Next taking $E^+(9, 18) = .7$ Mev, we get from (4.1)

$$E^-(8, 18) = -1.727 \text{ Mev} < 0,$$

i.e. O^{18} ought to be stable as is actually observed. In a similar manner the discussion may be continued for heavier members of the two groups.

C. The Group $I=4$. (Fig. 8, Table 7.)

This group extends from P^{34} to Ga^{66} . From the review of the methods of production given in Table 7, it appears possible to extend the group on both sides very considerably. On the left side, it appears possible to get Al^{30} , Na^{26} , F^{22} and N^{18} by (n, p) -reactions, e.g. N^{18} by the reaction $\text{O}^{18}(n, p)$, if the starting material could be concentrated. On the right side, it may be possible to prepare As^{70} , Br^{74} , Rb^{78} by (p, n) -reactions provided protons of sufficient energy are available, and the starting material, viz. Se^{74} (.9%), Kr^{78} (.35%), can be concentrated.

We first review the electron-emitters in details.

P^{34} : Giebert *et al.* (1944) have studied n -reactions with Cl and have identified a 14 sec. product with P^{34} . It shows a complex β -ray spectrum, 90% having the end-energy

of 5 Mev, and 10% having 3.2 Mev. The energy-release may be taken to be $E^- \simeq 5$ Mev.

Cl^{38} : The spectrum of this nucleus has been extensively investigated by Itoh (1941), Watase (1941) and Curran *et al.* (1940). Itoh has given a level scheme of Cl^{38} on the basis of these measurements which appear to be quite satisfactory. According to Itoh, the β^- -spectrum is a composite one of two components, having the end-energies of 4.99 Mev and 1.08 Mev. The difference is 3.91 Mev, which is the sum of the two observed γ -energies 2.19 Mev and 1.64 Mev. It appears therefore that the 1.08 Mev β -rays are emitted to an intermediate level, which descend to the lowest level of A^{38} after cascade emission of two successive γ -rays. The results of β - γ and γ - γ coincidence experiments of Watase are in agreement with these views. No spin-assignment of the levels has yet been made. Konopinski gives the 4.99 Mev-transition as of 2A-type, and 1.08 Mev-transition as of the allowed type. The maximum energy-release may be taken to be 4.99 Mev.

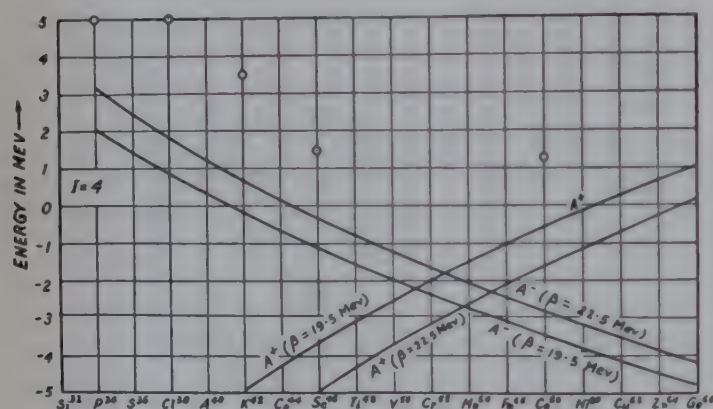


Fig. 8

K^{42} : This nucleus emits a β^- -spectrum whose end-energy has been fixed at 3.5 Mev by Kurie *et al.* (1936). It requires reinvestigation. The transition has been given to be of the 2A-type. We have taken the energy-release to be 3.5 Mev.

Sc^{46} : The disintegration-scheme of this long-lived nucleus (85-day) has been studied by Meitner (1945). She has shown that Sc^{46} emits a β^- -ray of end-energy 2.26 Mev which is followed by a γ -ray of 1.26 Mev energy. The energy-release in the transition $\text{Sc}^{46} \rightarrow \text{Ti}^{46}$ is therefore 1.51 Mev. She has disproved the earlier hypothesis of Mattauch and Flugge (Kernphysikalische Tabellen, 1942) that there is a second β -ray spectrum of end-energy 1.5 Mev. Meitner has also proved that Sc^{46} decays by K -capture to Ca^{46} . The ratio of K -capture to β^- -emission is given as 3:2, but the results are stated to be preliminary. We have $f^- \simeq 8$ for allowed transition and $f^- \cdot t \simeq 5.6 \times 10^6$. This ft -value is nearly 1,000 times larger than the allowed

ft -value. Hence actual f^- for this transition $\simeq 8 \times 10^{-4}$. We have $f^K \simeq 2\pi(\alpha Z)^3 \cdot (E^K/mc^2)^2 \simeq 2.5 \times 10^{-2} \cdot x^2$ if $E^K = x \cdot mc^2$. Taking $f^K/f^- = \frac{3}{2}$, we ought to have $f^K = 1.2 \times 10^{-3}$. So we get $x = \frac{1}{2}$ or 2 Mev.

V^{50} : Nothing is known about this nucleus except its life, which is given as 3.7 hrs. (Walke, 1937). It is not even known whether it emits β^- or β^+ -rays, or decays by K -capture and nothing is known of the end-energy of β -spectrum.

Let us now take up the β^+ -emitting and K -capturing nuclei.

Mn^{54} : This interesting nucleus, which has a long life of 310 days, decays only by K -capture, and positrons were not obtained, even though looked for. It emits a single γ -ray of energy 0.835 Mev which is due to an excited state of Cr^{54} . Deutsch and Elliot (1942) showed by coincidence experiments of the γ -ray, and the K_α -line of Cr^{54} which is the daughter nucleus, that every X-ray is followed by γ -ray. The K -capture therefore takes place in an excited level of Cr^{54} , but the energy-release to this excited level is not yet known.

Co^{58} : This nucleus which has been unambiguously identified as it has been produced by the reaction $\text{Mn}^{55}(\alpha, n)$ and has a life of 72 days. It was found by several workers to emit a positron-spectrum, and a γ -ray of energy 0.805 Mev in addition to the annihilation radiation of 0.505 Mev. The end-energy of the positron-spectrum which marks transition to an excited state of Fe^{58} was found to be 0.47 Mev. Deutsch and Elliot (1942) showed the ratio of $f^+/f^K \simeq 1$. This is in accordance with Fermi's theory of allowed transition. The γ -ray is from the excited state of Fe^{58} to a normal state. The energy-release in the transition $\text{Co}^{58} \rightarrow \text{Fe}^{58}$ is 1.275 Mev.

Discussion: Nuclei of this group give rise to some fundamental difficulties which may be grasped from the following representation (cf. Fig. 8a). It is generally found that in an arrangement of isobaric triplets as above, if

	Ca	Ti	Cr	Fe	Ni	
I = 6	(.0033%)	(5.34%)	(2.3%)	(.28%)	(3.8%)	
I = 4	$\downarrow K$	$\uparrow \downarrow$ Sc	$\circ V$	$\uparrow \downarrow$ Mn	$\uparrow \downarrow$ Co	$\uparrow \downarrow$ Cu
I = 2	Ca	Ti	Cr	Fe	Ni	
	(.64%)	(7.95%)	(4.49%)	(6.04%)	(57.4%)	
A	42	46	50	54	58	62

Fig. 8a

the isobars on the two extreme ends are stable, then the isobar in the middle is generally unstable showing of decay by both β^- -activity and β^+ -activity or K -capture.

We can easily verify from formulae (1.2) and (1.4) that this must be so. Thus

$$E^-(Z, A) = M(Z, A) - M(Z+1, A),$$

$$\text{and } E^K(Z+1, A) = M(Z+1, A) - M(Z, A) - m$$

$$\{1 - \sqrt{1 - \alpha^2 Z^2}\},$$

$$\simeq -E^-(Z, A) - \frac{1}{2}m\alpha^2 Z^2. \quad \dots (4.2)$$

Thus if the nucleus ${}_Z M^A$ is stable against β^- -decay, i.e. if $E^-(Z, A) < 0$, then

$$E^K(Z+1, A) > 0,$$

showing that the nucleus ${}_{Z+1} M^A$ ought to decay by K -capture unless of course if

$$-E^-(Z, A) < \frac{1}{2}m\alpha^2 Z^2, \quad (4.3)$$

in which case ${}_{Z+1} M^A$ may be stable against K -capture decay. But in general $\frac{1}{2}m\alpha^2 Z^2$ is of the order of a few thousand electron volts only so that the probability of (4.3) being satisfied is very small. If ${}_Z M^A$ is β^- -active, then ${}_{Z+1} M^A$ should be a stable nucleus. In Fig. 8 we find that apparently Mn^{54} , Co^{58} do not satisfy this rule, since these have not yet been found to decay by β^- -emission. If we take $\beta = 19.5$ Mev, then since $E^+(27, 58) = 1.275$ Mev, we have

$$E^-(27, 58) = -1.6 \text{ Mev}.$$

Thus Co^{58} should on no account decay by β^- -emission. In that case Ni^{58} should exhibit K -capture decay. But Ni^{58} is, as is well known, a very stable nucleus having a large abundance. Nothing is known about E^+ for Mn^{54} or V^{50} so that we cannot examine whether E^- for these nuclei can have positive values. If, however, we take $\beta = 22.5$ Mev, we find that

$$E^-(27, 58) = 0.55 \text{ Mev} > 0,$$

so that Co^{58} may emit extremely soft electrons to detect which we shall have to employ special technique. If we take $\beta = 22.5$ Mev we meet, however, another kind of difficulty. Taking the nucleus Sc^{46} , we have, provided $E^-(21, 46) = 1.52$ Mev,

$$(a) E^+(21, 46) = -0.996 \text{ Mev} > -2m, (\beta = 19.5 \text{ Mev}),$$

$$(b) E^+(21, 46) = -3.083 \text{ Mev} < -2m, (\beta = 22.5 \text{ Mev}).$$

Thus whereas for $\beta = 19.5$ Mev we can expect K -capture decay for Sc^{46} , $\beta = 22.5$ Mev will rule out any such possibility. It appears therefore necessary to repeat Meitner's work on Sc^{46} from this point of view and also examine Co^{58} for soft β^- -radiations. If the K -capture decay of Sc^{46} , which has been observed, is illusory then we cannot expect to have a stable Ca^{46} . The discovery of Ca^{46} and Ca^{48} has been claimed by Nier (1938) and their abundances have been given as .0033% and .2%. We shall take up this question again when we discuss Sc^{48} .

D. The Group $I=6$. (Fig. 9, Table 8.)

This group extends from the doubtful nucleus K^{44} to the stable nucleus Kr^{78} (.35%). The odd-odd nuclei are all unstable, but all have not yet been produced or studied. The methods of production are reviewed in Table 8. There are possibilities of extending the unstable nuclei on both flanks. It should certainly be possible to prepare Cl^{40} by the $\text{A}^{40} (n, p)$ -reaction and P^{36} by the $\text{S}^{36} (n, p)$ -reaction if S^{36} (abundance .016%) can be concentrated. It does not appear possible to go beyond P^{36} to Al^{32} . On the other flank, it should be possible to prepare Br^{76} , Rb^{80} , Y^{84} , Ma^{92} by Se^{76} (9.5%), Kr^{80} (2%), Sr^{84} (.56%) and Mo^{92} (41.9%) (p, n)-reactions if the target nuclei could be concentrated, and protons of sufficient energy can be obtained. The properties of these nuclei would be very useful for the testing of the theory because there are many

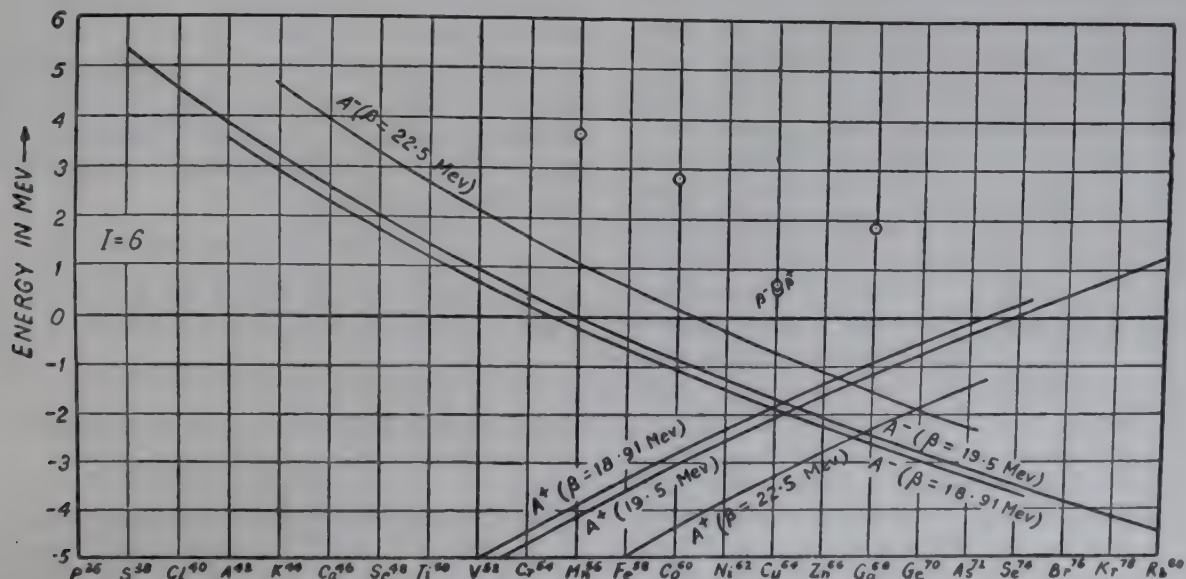


Fig. 9

lacunae in our knowledge of the group, which can be filled up only from data about the heavier nuclei. The knowledge of this group as a whole is rather too meagre.

Let us examine the β -emitters of this group one by one. The first radioactive nucleus reported is K^{44} , about which nothing is known, except a bare statement that it is β -emitting, with a life of 18 min.

Sc^{48} : The next nucleus Sc^{48} , having a life of 44 hrs., forms the subject of a paper by Hibdon and Pool (1945), and is reported to give a β -spectrum with end-energy of .57 Mev and a γ -ray of energy 1.35 Mev. The γ -ray is attributed to K -capture, the existence of which is not proved clearly, and it is said that 14 γ -rays are emitted per nuclear electron. We have reasons which we give later to differ very essentially from the conclusions of Hibdon and Pool.

V^{52} : We have no information about this nucleus except that it emits only γ -rays of energy 2.05 Mev.

Mn^{56} : This nucleus has been the subject of many investigations which have been summed up by Elliot and Deutsch (1943) where all references to older works would be found. They have given a level scheme which apparently explains all facts (Fig. 4a, p. 324 of their paper). Mn^{56} emits a composite β -spectrum which has been decomposed into three Fermi-curves with end-energies at .73 Mev, 1.05 Mev and 2.86 Mev, with the relative abundance of 15 : 25 : 60. Three γ -rays were observed with energies of .845 Mev, 1.81 Mev, 2.45 Mev. The γ -line .845 Mev is found also in the spectrum in Co^{56} which is a β^+ -emitting body, so that this level may be ascribed to Fe^{56} to which both Mn^{56} and Co^{56} decay. The energy-release in the transition $Mn^{56} \rightarrow Fe^{56}$ is given as 3.705 Mev. This has been accepted in this paper. No spin-assignment to these levels has yet been made. No positron-emission or K -capture is reported.

Co^{60} : This is a very interesting β -emitting nucleus consisting of two isomers, having lives of 5.3 yrs. and 10.7 min. respectively. Many level schemes have been given but it will suffice to mention that of Deutsch *et al.* (1945), who have given references to earlier papers. Each isomer has its own β -spectrum and γ -rays. The 5.3 yrs. Co^{60} emits a positron-spectrum with end-energy which is given as .3 Mev by Deutsch *et al.* and .23 Mev by Das and Saha (1946). This is followed by γ -rays of energy 1.10 Mev and 1.30 Mev. The 10.7 min. Co^{60} emits a β -spectrum with end-energy of 1.28 Mev, followed by a single γ -ray of energy 1.5 Mev. There is besides a γ -ray of energy .056 Mev which is very strongly converted. It is assured on plausible grounds that 90% of the 10.7 min. Co^{60} decays by the emission of .056 Mev γ -ray to the 5.3 yrs. Co^{60} . It cannot yet be said that the level schemes have been well worked out. According to these works, however, the energy-release in the transition $Co^{60} \rightarrow Ni^{60}$ appears to be ≈ 2.8 Mev. There is no evidence yet of β^+ -emission or K -capture decay by this nucleus.

Cu^{64} : This was the first nucleus which was found to emit both β^- and β^+ rays and almost in equal proportion but Cl^{36} was found later to emit also simultaneously electrons and positrons. Both the positron and negatron spectra were very carefully investigated by Tyler (1939) in his precision magnetic spectrometer, and found to yield simple allowed type of Fermi spectra with end-energies at .659 Mev and .578 Mev respectively. There is departure from the ideal form on the low-energy side which is greater for the positron than for the electron-spectrum. These points were recently investigated by Backus (1946), who found actually a larger number of positrons on the low-energy side (below .5 Mev) than one can get from the Fermi theory. On the whole, the evidence so far available does not enable us to postulate the existence of any γ -ray from Cu^{64} , but as it is expected to decay by K -capture, γ -rays may be emitted. Using the standard formula, we get f^K/f^+ for $Cu^{64} = 2.26$, and an investigation by Bradt *et al.* (1945) gives for the ratio of Ni-K quanta to annihilation radiation from Cu^{64} , the value 1.82. From experiments on γ - γ coincidence, the above authors find no γ -ray from Cu^{64} . Assuming that $E^- = .58$ Mev and $E^+ = .66$ Mev for Cu^{64} , we can apply formula (4.1) to calculate β . We find that

$$\beta \approx 18.91 \text{ Mev.}$$

The value of β is now the standard value (cf. §1).

Ga^{68} : The cloud-chamber investigation of spectrum of Ga^{68} (Mann, 1937) has shown the energy of the positron-spectrum to be 1.86 Mev. Ga^{68} is also expected to emit β^- -particles of small energy, but no such rays are known, and if stable Ge^{68} does not exist, Ga^{68} cannot be β^- -emitting. But it is one of the border line cases and ought to be more carefully investigated.

Discussion: We have seen that if E^+ and E^- for Cu^{64} are taken as .66 Mev and .58 Mev respectively then β should have the value 18.91 Mev. We have drawn in Fig. 9 the $A^\pm$ -curves for the group with three values of β , viz. $\beta = 18.91$ Mev, 19.5 Mev and 22.5 Mev. $\beta = 18.91$ Mev, though explaining the energetics of Cu^{64} , presents us with certain serious difficulties. Taking $E^-(25, 56) = 3.705$ Mev, we have from equation (4.1)

$$E^+(25, 56) = .106 \text{ Mev,}$$

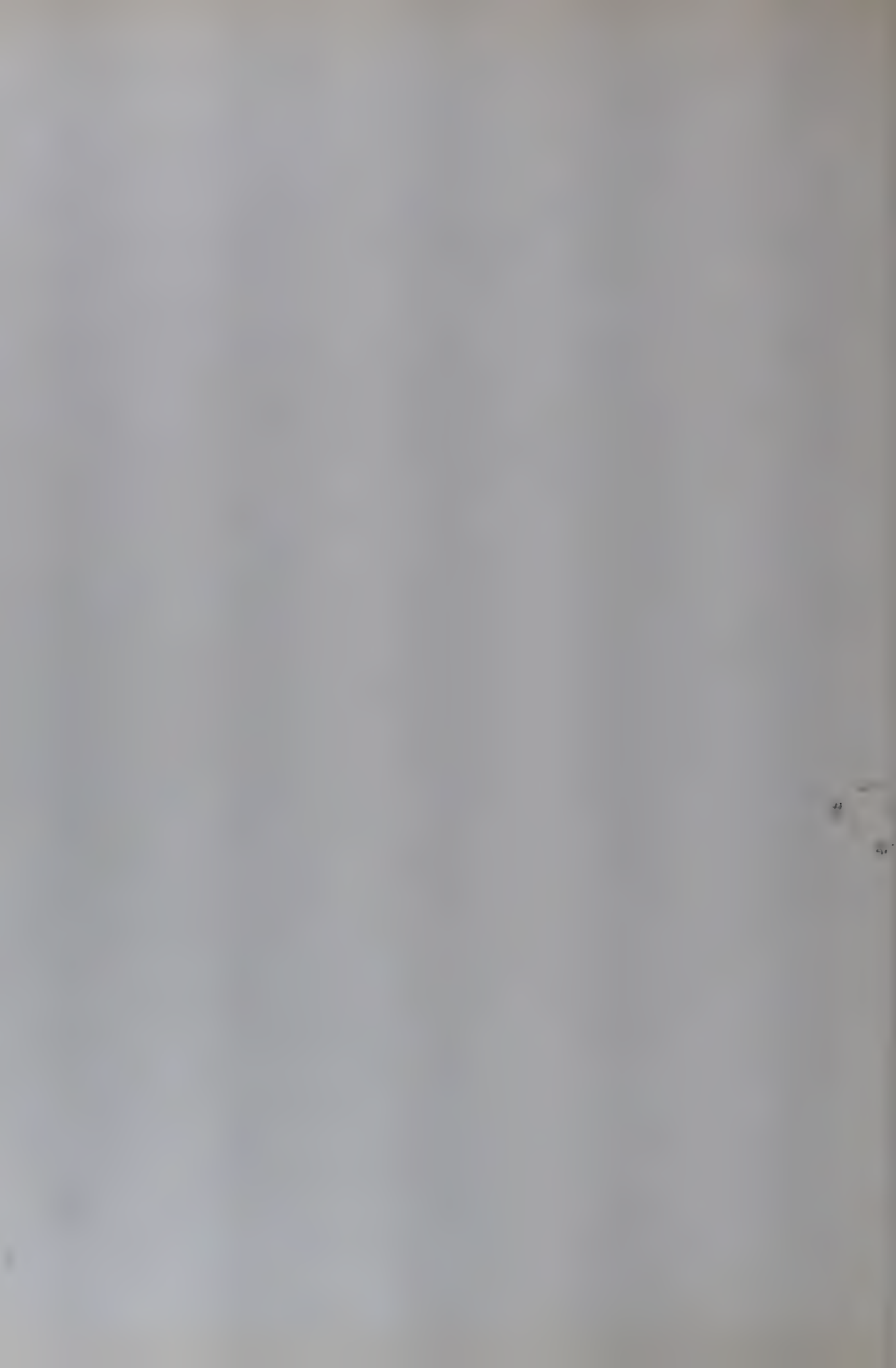
so that Mn^{56} should decay by K -capture as well as β^+ -emission. Similarly taking $E^-(27, 60) = 2.8$ Mev, we get

$$E^+(27, 60) = 1.124 \text{ Mev,}$$

and if we take $E^+(31, 68) = 1.86$ Mev, we get

$$E^-(31, 68) = .138 \text{ Mev.}$$

We find therefore Co^{60} ought to exhibit β^+ -decay as well as decay by K -capture, whereas Ga^{68} should decay by β^- -emission. None of these statements are borne out by observations. We therefore try $\beta = 22.5$ Mev which has



been so successful for the preceding groups. We get then

$$E^+(25, 56) = -2.97 \text{ Mev}, E^+(27, 60) = -1.748 \text{ Mev},$$

$$E^-(31, 68) = 2.672 \text{ Mev},$$

so that the stability of Mn^{56} and Co^{60} against decay by K -capture or β^+ -decay is well explained, although we find that Ga^{68} should decay by β^- -emission. The investigations of Mn^{56} and Co^{60} appear to be thorough while that of Ga^{68} is not of the same standard. The product nucleus of a possible β^- -decay process of Ga^{68} , viz. Ge^{68} is, however, not known. For Cu^{61} if we take $E^-(29, 64) = 578 \text{ Mev}$ as correct then

$$E^+(29, 64) = -2.026 \text{ Mev},$$

so that Cu^{61} should not exhibit β^+ -emission or K -capture. On the other hand, if we take $E^+(29, 64) = 659 \text{ Mev}$ as correct then we get

$$E^-(29, 64) = 3.263 \text{ Mev}.$$

Thus the energy 2.685 Mev should be emitted as γ -rays. It may be quite possible that a number γ -rays of approximate energy 5 Mev are emitted in cascades. It would be difficult to detect them unambiguously on account of the presence of annihilation radiation.

It is therefore seen that all the nuclei, except Sc^{48} and perhaps Ga^{68} , conform in a general way to our scheme. Sc^{48} , however, is a glaring anomaly and we proceed to consider this nucleus carefully. As Sc^{48} is placed between the stable nuclei Ti^{48} (abundance 73.45%) and Ca^{48} (abundance 19%), both K -capture and β^- -emission must take place if Ca^{48} really exists. Ca^{48} belongs to the group $I=8$, which starts from stable Ca^{48} . After Ca^{48} , however, there is a long gap and the nuclei Ti^{52} and Cr^{56} which may be expected to be stable are not found. None of the expected isotopes are obtained until we come to Ni^{60} (88%). The artificially produced nuclei of the group $I=6$ after Sc^{48} are V^{52} , Mn^{56} , Co^{60} . V^{52} as already mentioned is not well-investigated but Mn^{56} , Co^{60} have been very thoroughly studied. It is therefore surprising that while Mn^{56} , Co^{60} do not decay by K -capture or β^+ -emission, Sc^{48} does so. Let us examine Sc^{48} on the basis of our theory. If β is taken to be 22.5 Mev, then $A^+(21, 48) = -8.374 \text{ Mev}$, so that if Sc^{48} shows K -capture we must have

$$-\chi(21, 48) > 7.352 \text{ Mev}.$$

In the case, however, $E^-(21, 48)$ should have a relatively high value, viz.

$$E^-(21, 48) > 10.628 \text{ Mev}$$

which is not borne out at all by observations. The whole tangle can be solved at one stroke if we assume that a stable Ca^{48} does not exist. Nier (1938) who claimed to have found evidence for Ca^{48} and Ca^{46} in his mass-spectrograph had apparently some doubt whether these mass-numbers were really due to Ca and gave a discussion on these points. Apparently he satisfied himself that these isotopes of Ca do

exist. Our suggestion is that γ -ray reported from Sc^{46} are not due to K -capture but are emitted in cascades after β^- -emission. In that case the E^- energy-release in the transition $\text{Sc}^{48} \rightarrow \text{Ti}^{48}$ would be quite large. This suggestion was made by Pollard (1938), but has been rejected by Hibdon *et al.* But since other nuclei of this group, viz. Mn^{56} , Co^{60} , emit very soft β^- -rays followed by a large number of γ -rays in cascade, we may expect the same kind of process for Sc^{48} . After this paper was written we came across a paper by Curie (1945) who is also of the opinion that there cannot be any stable Ca^{48} .

Conclusion: We have thus found that β -activity of nuclei may be neatly explained by the inclusion of a spin-dependent term in the Weizsäcker-Bethe mass-defect formula. We have not as yet arrived at any analytic dependence of this term $\chi(Z, A)$ on the spin or the magnetic moment of the nucleus (Z, A) . It appears from the above discussion that $\chi(Z, A)$ is generally of the order of a few million electron volts. According to classical theory, it should, however, be $\simeq \frac{Zev}{cr^2} \mu_N$, where v = velocity of a nucleon inside the nucleus, μ_N = the magnetic moment of the nucleus, and r = the nuclear radius. Making plausible assumptions regarding these quantities, we find that $\frac{Zev}{cr^2}$ should be of order of 10 kiloelectronvolts. This shows that we have to consider some type of meson theory to find out the right order of value of the spin-dependent part of the nuclear binding energy.

It is a pleasure to thank Mr. S. N. Ghosal, M.Sc., for his kind assistance in the preparation of the graphs and tables appearing in this paper. The discussions for the groups beyond $I=6$ will be found in a paper by Saha Jr. and Ghoshal to be published soon.

REFERENCES

- ALLEN, POOL, KURBATOV and QUILL (1941). Artificial radioactivity of Ti^{48} . *Phys. Rev.*, **60**, 425.
 ALVAREZ (1938). The capture of orbital electrons by nuclei. *Phys. Rev.*, **54**, 486.
 ASTON (1942). Mass-spectra and isotopes. E. Arnold & Co., London.
 BACKUS (1946). The β -rays of Cu^{64} at low energies. *Phys. Rev.*, **68**, 59.
 BARKAS (1939). The analysis of nuclear binding energies. *Phys. Rev.*, **55**, 691.
 BAYLEY and CRANE (1937). The β -ray spectra of Li^8 and B^{12} . *Phys. Rev.*, **52**, 604.
 BETHE and BACHER (1936). Nuclear physics. *Rev. Mod. Phys.*, **8**, 90.
 BETHE and HENDERSON (1939). Evidence for incorrect assignment of the supposed Si^{37} radioactivity of 6.7 min. half life. *Phys. Rev.*, **56**, 1060.
 BIRGE (1941). The general physical constants. *Rep. Prog. Phys.*, **8**, 90.
 BJERGE and BROSTRÖM (1936). β -ray spectrum of radio-He. *Nat.*, **38**, 400.
 BOHR and WHEELER (1939). The mechanism of nuclear fission. *Phys. Rev.*, **56**, 426.
 BOWER and BURCHAM (1940). Experiments on the transmutation of F by deuterons. *Proc. Roy. Soc. Lond., A*, **173**, 379.

- BRADT *et al.* (1944) and (1945). *Helv. Phys. Acta*.
- BREIT and KNIPP (1938). Note on electron capture in Be^7 . *Phys. Rev.*, **54**, 652.
- CORK, HADLEY and KENT (1942). Relative probability of $(d, 2n)$ -reaction in Ni and Zn. *Phys. Rev.*, **61**, 388.
- CRITTENDEN (1939). The β -ray spectra of Mg^{27} , Cu^{63} and the nuclear isomers of Rh^{104} . *Phys. Rev.*, **56**, 709.
- CURAN, DEE and STROTHERS (1940). Some measurements of β -ray energies. *Proc. Roy. Soc. Lond.*, A, **174**, 546.
- CURIE (1945). Empirical determination of the atomic number Z_A corresponding to the maximum stability of atoms of mass A . *Jour. Phy. Rad. Series* 8, **6**, 209.
- CURTIS (1939). The γ -radiations from radioactive Co. *Phys. Rev.*, **55**, 1136.
- DAS and SAHA (1946). Radioactivity of 5.3 year Co^{60} . *Proc. Nat. Inst. Sci.* (in course of publication).
- DELSASSO, RIDENOUR, SHERR and WHITE (1939). Artificial radioactivity produced by proton. *Phys. Rev.*, **55**, 113.
- DEMPSTER (1936). Energy Content of Heavy Nuclei. *Phys. Rev.*, **53**, 869.
- DEUTSCH and ELLIOT (1942). Disintegration schemes of radioactive substances. VII. Mn^{54} and Co^{58} . *Phys. Rev.*, **65**, 211.
- DEUTSCH, ELLIOT and ROBERTS (1945). Disintegration schemes of radioactive substances. VIII. Co^{60} . *Phys. Rev.*, **68**, 193.
- DORAN and HENDERSON (1941). New reactions in Ni. *Phys. Rev.*, **60**, 411.
- DUCKWORTH (1942). New packing fraction curves. *Phys. Rev.*, **62**, 19.
- ELLIOT and DEUTSCH (1943). Disintegration schemes of radioactive substances. VI. Mn^{55} and Co^{59} . *Phys. Rev.*, **64**, 321.
- ELLIOT and KING (1941). Radioactive Sc^{41} , A^{88} and S^{31} . *Phys. Rev.*, **59**, 403.
- GIEBERT, ROGGEN and ROSSEL (1944). Nuclear reactions of chlorine with neutrons. *Helv. Phys. Acta.*, **17**, 97.
- GRAHAME and WALKER (1941). Preparation and properties of long-lived radio-chlorine. *Phys. Rev.*, **60**, 909.
- GRAVES (1939). Packing fraction differences among heavy elements. *Phys. Rev.*, **55**, 863.
- HAXBY, SHOUPP, STEPHENS and WELLS (1940). Thresholds for proton-neutron reactions of Li, Be, B and C. *Phys. Rev.*, **58**, 1035.
- HEMMENDINGER (1940). Proton induced activity of Mn. *Phys. Rev.*, **58**, 929.
- HENDERSON (1935). *Phys. Rev.*, **48**, 855.
- HENDERSON (1938). The energy of the β -rays from K. *Phys. Rev.*, **55**, 238.
- HIBDON, POOL and KURBATOV (1944). Radioactivity of V. *Bul. Amer. Phys. Soc.*, **19** (No. 2), 13.
- HIBDON, POOL and KURBATOV (1944). Transmutation of Ti. *Phys. Rev.*, **65**, 351.
- HIBDON, POOL and KURBATOV (1945). Radioactive Sc. I. *Phys. Rev.*, **67**, 289.
- HIBDON and POOL (1945). Radioactive Sc. II. *Phys. Rev.*, **67**, 313.
- HUBER, LIENARD, SCHERRER and WÄFFLER (1943). *Helv. Phys. Acta.*, **16**, 146; **16**, 431.
- HUBER, LIENARD, SCHERRER and WÄFFLER (1944). *Helv. Phys. Acta.*, **17**, 224.
- ITO (1941). Radioactivity of Cl^{38} . *Proc. Phys. Math. Soc. Jap.*, **23**, 605.
- KAMEN (1941). Production and isotopic assignment of long-lived radioactive sulphur. *Phys. Rev.*, **60**, 537.
- KLEMPERER (1934). Radioactivity of K and Rb. *Proc. Roy. Soc. Lond.*, A, **148**, 638.
- KONOPINSKI (1943). β -decay. *Rev. Mod. Phys.*, **15**, 209.
- KRÜGER and OGLE (1945). γ -rays emitted during radioactive transitions. *Phys. Rev.*, **67**, 273.
- KURIE, RICHARDSON and PAXTON (1936). Radiations emitted from artificially produced bodies radioactive substances. Part I. Upper limits and shapes of β -ray spectra for several elements. *Phys. Rev.*, **49**, 368.
- LAWSON (1939). The β -ray spectra of P, Na and Co. *Phys. Rev.*, **56**, 131.
- LIBBY and LEE (1939). Energies of soft β -radiations of Rb and other bodies, method of their determination. *Phys. Rev.*, **55**, 245.
- LIVINGOOD and SEABORG (1938). Radioisotopes of Ni. *Phys. Rev.*, **53**, 765.
- LIVINGOOD and SEABORG (1938). Radioactive Mn isotopes. *Phys. Rev.*, **54**, 391.
- LIVINGOOD and SEABORG (1939). Longlived radioactive Fe^{65} . *Phys. Rev.*, **55**, 1268.
- LIVINGOOD and SEABORG (1940). Table of induced radioactivities. *Rev. Mod. Phys.*, **12**, 30.
- LIVINGOOD and SEABORG (1941). Radioactive isotopes of Co. *Phys. Rev.*, **60**, 913.
- MAGNAN (1941). Radioactivity of P^{30} . *Ann. d. Phys.*, **15**, 5.
- MAIER-LEIBNITZ (1944). Coincidence measurements of radioactive Na isotopes. *Zeits. Phys.*, **122**, 233.
- MANN (1937). Nuclear transformation in Cu. *Phys. Rev.*, **52**, 405.
- MATTAUCH and FLÜGGE (1942). Isotopenbericht, Berlin.
- MEITNER (1945). On the radioactivity of Sc^{44} . *Arkiv. Math. Phys.*, **32**, 2.
- MÖLLER (1937). On the capture of optical electrons by nuclei. *Phys. Rev.*, **51**, 84.
- NELSON, POOL and KURBATOV (1941). Radioactive isotopes of Ni. *Phys. Rev.*, **61**, 428.
- NIELSON (1941). Energy spectrum of H^3 β -rays. *Phys. Rev.*, **60**, 160.
- NIER (1938). The isotopic constitution of Ca, Ti, S and A. *Phys. Rev.*, **53**, 282.
- NORDHEIM and YOST (1937). On the matrix element in Fermi's theory of β -decay. *Phys. Rev.*, **51**, 942.
- O'Connor, Pool and Kurbatov (1941). Artificial radioactivity of Cr^{48} . *Phys. Rev.*, **62**, 413.
- PLESSET (1941). Nuclear excitations resulting from radioactive decay. *Phys. Rev.*, **62**, 181.
- POLLARD (1938). Transmutation of Sc by ThC-particles. *Phys. Rev.*, **54**, 411.
- RICHARDSON and KURIE (1936). The radiations emitted from artificially produced radioactive substances. II. γ -rays from several elements. *Phys. Rev.*, **50**, 999.
- RIDENOUR and HENDERSON (1937). Artificial radioactivity produced by α -particles. *Phys. Rev.*, **52**, 889.
- RUBEN and KAMEN (1940). Long-lived radioactive C. *Phys. Rev.*, **59**, 349.
- SAHA, A. K. (1944). The theory of the screen cathode β -ray spectrometer. *Proc. Nat. Inst. Sci. Ind.*, **10**, 355.
- SAHA, A. K. (1946). Radioactivity of S^{35} , Rb^{87} and RaD . *Proc. Nat. Inst. Sci. Ind.*, **12**, 159.
- SAHA, M. N., SARKAR and MUKHERJEE (1940). On the structure of atomic nucleus. *Proc. Nat. Inst. Sci. Ind.*, **6**, 45.
- SEABORG (1944). Table of isotopes. *Rev. Mod. Phys.*, **16**, 1.
- SOMMERS (JR.) and SCHERR (1946). Activity of N^{16} and He^6 . *Phys. Rev.*, **69**, 2.
- THOMPSON and HOLT (1944). Radioactivity of K^{40} . *Nat.*, **153**, 103.
- TOWNSEND (1941). β -spectra of light elements. *Proc. Roy. Soc. Lond.*, A, **177**, 357.
- TURNER (1940). Nuclear fission. *Rev. Mod. Phys.*, **12**, 1.
- TURNER (1940). Radioactive isotopes of V. *Phys. Rev.*, **58**, 179.
- TYLER (1939). β - and γ -radiations from Cu^{64} and Eu^{152} . *Phys. Rev.*, **56**, 125.
- THOMPSON and ROWLANDS (1943). *Nat.*, **152**, 103.
- WALKE (1937). Induced radioactivity of Ti and V. *Phys. Rev.*, **52**, 777.

WALKE, THOMPSON and HOLT (1940). K -capture and internal conversion in Cr^{51} . *Phy. Rev.*, **57**, 171.

WALKE, THOMPSON and HOLT (1940). Radioactive isotopes of Ca and their suitability as indicator. *Phy. Rev.*, **57**, 177.

WATASE (1940). On the disintegration of N^{13} nucleus. *Proc. Phy. Math. Soc. Jap.*, **22**, 639.

WATASE (1941). *Proc. Phy. Math. Soc. Jap.*, **23**, 618.

WATASE, ITOH and TAKADA (1940). Radiations from radioactive Zn^{65} . *Proc. Phy. Math. Soc. Jap.*, **22**, 90.

WEIMER, KURBATOV and POOL (1941). Radioactive argon A^{37} . *Phy. Rev.*, **60**, 469.

WEIZSÄCKER (1935). On the theory of nuclear masses. *Zeits. Phys.*, **96**, 431.

WHITE, CREUTZ, DELSASSO and WILSON (1941). Positrons from light nuclei. *Phy. Rev.*, **59**, 63.

WHITE, DELSASSO, FOX and CREUTZ (1939). Short-lived radioactivities induced in F, Na, and Mg by high energy protons. *Phy. Rev.*, **56**, 512.

WIDDOWSON and CHAMPION (1938). Upper limits of continuous β -ray spectra. *Proc. Roy. Soc. Lond.*, **A**, **50**, 185.

WIGNER and FEENBERG (1941). Symmetry properties of nuclear levels. *Rep. Prog. Phys.*, **8**, 274.

YASAKI and WATANABE (1938). Deuteron induced radioactivity in O. *Nat.*, **141**, 787.

YUKAWA and SAKATA (1935). On the interaction of heavy particle I. *Proc. Phys. Math. Soc. Jap.*, **17**, 48.

ZACHARIAS (1941). Nuclear spin and magnetic moment of K^{40} . *Phy. Rev.*, **61**, 270.

78. ON NUCLEAR ENERGETICS AND BETA-ACTIVITY*

M. N. SAHA AND A. K. SAHA

(*Nature*, **158**, 6, 1946)

Ever since the discovery by Joliot and Curie of the phenomenon of induced radioactivity in 1934, a very large number of radioactive nuclei, exceeding 450, has been prepared in the laboratory. In recent years, new types of radioactive nuclei have been obtained from fission of heavy nuclei like ${}_{92}\text{U}$, ${}_{90}\text{Th}$ and ${}_{91}\text{Pa}$, and possibly also of ${}_{93}\text{Np}$ and ${}_{94}\text{Pu}$; which have, however, not yet been released for publication. Extensive studies of the β^- and β^+ activities of these nuclei have been made in the various laboratories of the world. The data so far collected, though they have reached vast magnitudes, are by no means sufficient, but already they form a rather bewildering mass (for example, see tables by Seaborg¹), reminding one of the vast collection of spectroscopical data, before the rise of the modern theories of the electron-structure of the atom reduced them to a few simple laws like Pauli's exclusion principle.

In addition to the nuclei like C^{14} which have been prepared in the laboratory, we have nuclei, mostly stable, occurring in Nature the number of which now reach nearly 250. In the case of nuclei derived from fission, the designation of a new isotope by mass is occasionally not quite unambiguous; indeed, this is a very acute problem for fission products.

Several attempts at a regularization of data have been made by previous workers, but here we shall refer to a chart prepared by Saha, Sarkar and Mukherjee², a section of which is shown in Fig. 1; the full chart is too large to be reproduced here. This is a synthesis of several charts

already published by different authors. In this, the abscissa represents mass-number M , the ordinate represents the isotope number $I=N-Z$, which represents the excess of neutrons over protons in any nucleus. M ranges from 1 to 239, and I from -1 to about 54. The section of the chart reproduced here extends from $I=-1$ to $I=8$. We have attempted to make the chart as up to date as possible. The parallel lines at 45° , henceforth to be called the Z -lines, represent the atomic number Z . Thus all isotopes of the element Z are to be found on the same Z -line. Each isotope is represented by a circle. Solid circles, $\bullet$, represent 'stable nuclei'. Hollow circles, $\circ$, with an arrow pointing upwards represent β^+ - (positron)-emitting nuclei. When the arrow points down, ϕ , it indicates that the nucleus is β^- - (electron)-emitting. Circles with arrow pointing both up and down, ϕ , indicate that the nucleus emits both neutrons and positrons, for example, Cu^{64} . δ denotes that the nucleus decays by K -capture only. $\circ$ denotes that

the nucleus decays by K -capture as well as by positron-emission. ϕ denotes that the nucleus has been obtained in 'fission'; such nuclei are all β^- -emitting. If any particular isotope has two different half-lives (isomers), both half-lives are given (compare Co^{60}). Saha, Sirkar and Mukherjee² gave the following rules of stability, some of which were previously known:

Rule 1: I is even.

When I is even, say 4, we get alternation of stable and β -active nuclei, as shown below:

Z : 15*	16	17	18	19	20	21	22	23	24	25	26	27
P^{34}	S^{36}	K^{38}	A^{40}	K	Ca^{44}	Sc^{46}	Ti^{48}	V^{50}	Cr^{52}	Mn^{54}	Fe^{56}	Co^{58}
—	S	—	S	—	S	—	S	—	S	—	S	+

*Summary of a paper by M. N. Saha and A. K. Saha, "On Nuclear Energetics and β -Activity," *Trans. Nat. Inst. Sci. India*, **2**, 193 (1946.)

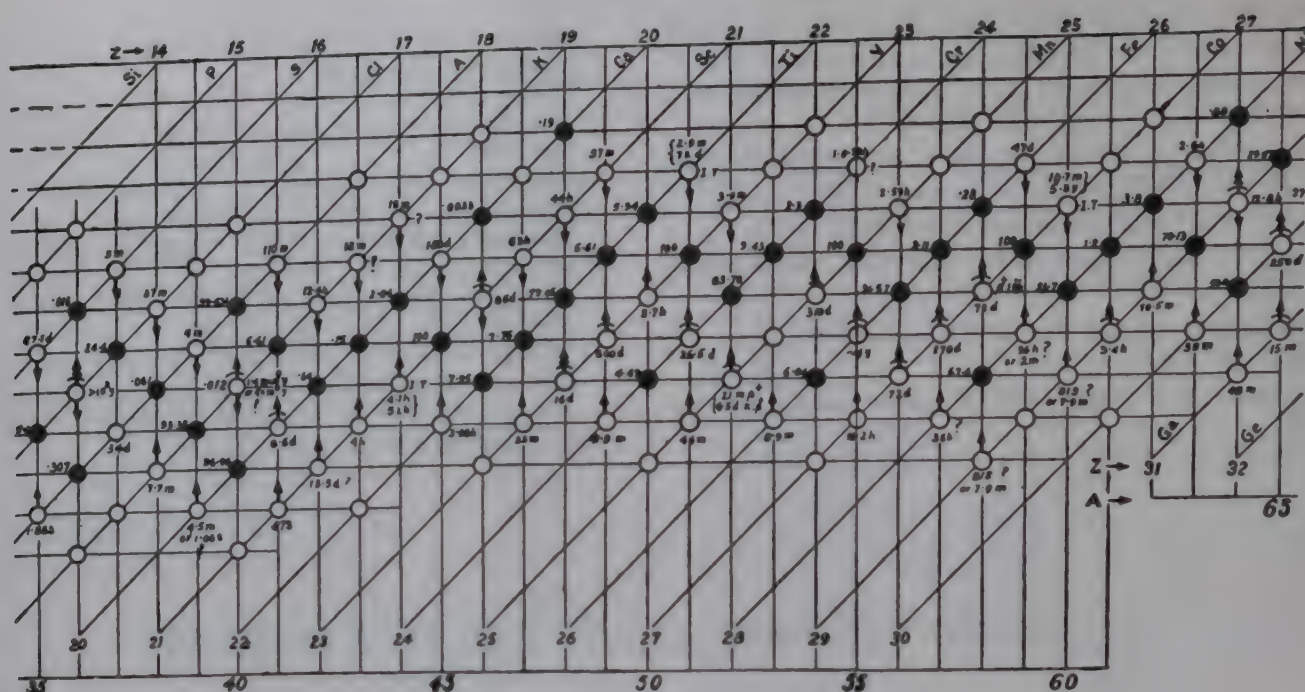


Fig. 1

S denotes stable, — denotes negatron-emitting, + denotes positron-emitting.

Exceptions. There are certain exceptions:

(a) He^6 , B^{10} , C^{14} are β -active, though both N and Z are even. (b) H^4 , Li^6 , B^{10} , N^{14} are stable, though both N and Z are odd. These rules have been given by Bethe and others.

Rule 2. I is odd, say 5: We have

Z:	18	19	20	21	22	23	24	25	26	27	28	29
	Ar^{41}	K^{43}	Ca^{45}	Sc^{47}	Ti^{49}	V^{51}	Cr^{53}	Mn^{55}	Fe^{57}	Co^{59}	Ni^{61}	Cu^{63}
	—	—	—	—	—	—	—	—	—	—	—	—
	30	31	32	33	Stable							
	Zn^{65}	Ga^{67}	Ge^{69}	As^{71}								
	+	+	+	+								

(—) denotes negatron-emitting, (+) denotes positron-emitting.

The above is illustrative of all groups having I odd. If in any of the odd groups we arrange the nuclei in order of their mass numbers Z , we first get β -emitting nuclei, then a succession of stable nuclei, which are followed by β^+ -emitting nuclei.

These rules apply only to known nuclei. If in future it be possible to extend the series on both flanks, will the new nuclei follow these rules? We need not consider the nuclei with odd I because evidently rule 2 will continue to apply to them. Let us consider nuclei with I even: they may be illustrated by a typical group, say $I=4$; we may think of the possibility of forming some day in the laboratory $_{12}\text{Mg}^{28}$ and $_{14}\text{Si}^{32}$, on the left flank, and $_{32}\text{Ge}^{68}$, $_{34}\text{Se}^{72}$, on the right flank, though these are at

present unknown. Will they be stable, or unstable like $_{6}\text{C}^{14}$ with a long life?

An explanation to these rules, and a clue to the energetics of β -emission, is afforded in a general way if we write out the formula for mass-defect of nuclei in the form $\Delta M(Z, A) = \varphi(Z, A) + \chi(Z, A)$, where $\varphi(Z, A)$ is the spin-independent part, which is given by one of the various mass-defect formulae due to Weizsäcker, Bethe or Wigner. We have taken, for the sake of simplicity, the Weizsäcker-

$$\text{Bethe form } \varphi(Z, A) = aA - \beta \frac{I^2}{A} - \gamma A^{\frac{1}{2}} - \frac{\delta Z^2}{A^{\frac{1}{2}}} \quad (1)$$

with Bethe's values of the constants a , β , γ , δ . These values were based on older data on masses of nuclei, but probably the newer data will give better values. But these have not been available to us. We have sometimes adjusted the value of β , but this is an unsatisfactory procedure from the theoretical point of view. The Weizsäcker-Bethe formula holds only for Z even, N even, for which the nuclear spin $i=0$, and the spin-dependent term $\chi(Z, A)=0$.

THE SPIN-DEPENDENT TERM

When I is even and Z odd, N odd, for example, in $_{7}\text{N}^{16}$, we have found uniformly that $\chi(Z, A)$ is negative and of the order of a few million electron-volts. For odd I , no general principle has yet been found.

From the general mass-defect formula, expressions for the energy-release in β -transitions have been worked out. Let E^- be total energy-release in a β -transition in

which a nucleus ${}_Z M^A$ changes to ${}_{Z+1} M^A$; then it can be easily shown that

$$E^- = A^- + \chi(Z+1, A) - \chi(Z, A),$$

where

$$A^- = 0.766 + \frac{4\beta(I-1)}{A} - \frac{\delta(A-I+1)}{A^{\frac{1}{2}}} \quad \text{in Mev.} \quad (2)$$

The χ -functions may be multi-valued, corresponding to the different nuclear levels of both parent and daughter nuclei. For β^+ -emission, let us denote by E^+ the total energy-release in a β^+ -transition when the nucleus ${}_Z M^A$ changes to ${}_{Z-1} M^A$. It can be easily shown that

$$E^+ = A^+ + \chi(Z-1, A) - \chi(Z, A),$$

where A^+ is the spin-independent part given by

$$A^+ = -1.788 - \frac{4\beta(I+1)}{A} + \frac{\delta(A-I-1)}{A^{\frac{1}{2}}}. \quad (3)$$

For K -capture, the energy E^K released in the process, which is taken to be carried by the neutrino, is given by

$$E^K = E^+ + mc^2 \{1 + \sqrt{1 - \alpha^2 Z^2}\} \simeq E^+ + 2mc^2. \quad (4)$$

ENERGY-RELEASE

In cases where the β -transitions are of a simple allowed type, the energy-release is simply equivalent to the end-energy of the β -spectrum, for in general in such cases no γ -rays are emitted. Where such is not the case, but β -rays are of the forbidden type, for example, in Na^{24} , and γ -rays are also emitted, the task of finding the energy-release from the β - and γ -radiations emitted is a rather

difficult one, and every case has to be dealt with separately. A typical case is afforded by Na^{24} , which has been discussed by Krüger and Ogle³ and by Maier-Leibnitz⁴. In such cases we have to examine with great care the decay scheme of the β -transitions as given by different authors; but this is not easy, for the data are very often contradictory.

According to these formulae, the values of E^- , E^+ and E^K depend on I and A , and on the spin-dependent terms $\chi(Z, A)$. The classification of nuclei according to I -values is therefore justified.

It is obvious that a nucleus is stable with respect to β^- -emission when E^- is negative, and with respect to β^+ -emission when E^+ is negative. But for the right hand nuclei of the nuclear chart, even when E^+ is negative, the nuclei may decay by K -capture, provided E^K is greater than 0, or E^+ is greater than $-2mc^2$, which is approximately 1 Mev. The line of stability is therefore depressed by -1 Mev. below the zero-line, for the right-hand nuclei.

The operation of these rules is best illustrated by taking one or two typical examples for I odd and I even separately. We first take I odd, and choose the group $I=3$. This is illustrated in Fig. 2. Here the abscissa represents the mass number M , the ordinate represents A^- and A^+ , calculated from formulae (2), (3). The known nuclei extend from O^{19} to Ga^{65} . If the χ -terms contributed nothing to E^- or E^+ , all nuclei for which A^- -values were below the zero-line, and A^+ -values below the line (-1) would have been stable, namely, from S^{35} to Ti^{47} , and the energy-release would be given by the values of A^- and A^+ against each mass number.

Actually we have all nuclei from Cl^{37} to Ti^{47} stable, with the exception of A^{39} , about which we have extremely meagre data and probably wrong information. S^{35} is very

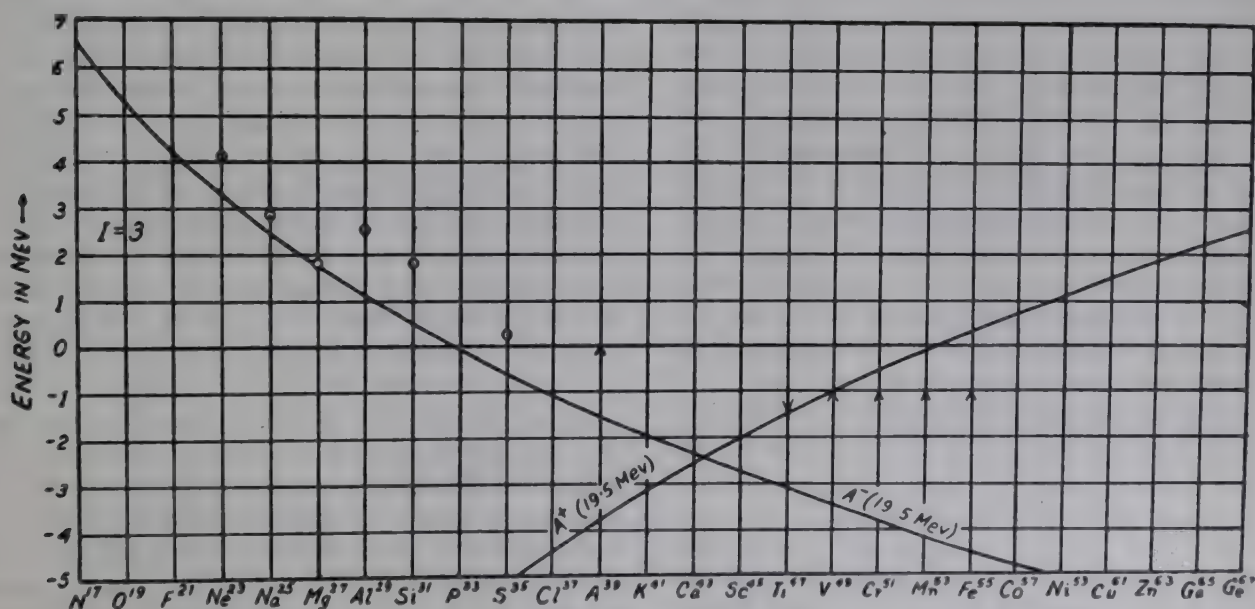


Fig. 2

nearly stable—it has a long life of 87.5 days. We have for S^{35} ,

$$E^- = A^- + \chi(18, 35) - \chi(17, 35).$$

The A^- is below the zero line, $\chi(18, 35) - \chi(17, 35)$ is evidently positive, and these terms take E^- slightly above the zero line. E^- is only 0.103 Mev. according to the measurements of one of us (A. K. Saha), but if there is a γ -ray emitted by S^{35} in cascade, as claimed by Giebert *et al.*⁵, E^- is 0.233 Mev.

2. *Odd-odd nuclei* (N odd, Z odd). For such nuclei we have, since Z is odd,

$$E^- = A^- - \chi(Z, A) > A^-,$$

$$E^+ = A^+ - \chi(Z, A) > A^+ \quad \dots (6)$$

The operation of these rules is illustrated by the case $I=2$.

The known nuclei for $I=2$ range from He^6 to Ga^{64} and the operation of rules (2), (3) is illustrated in Fig. 3.

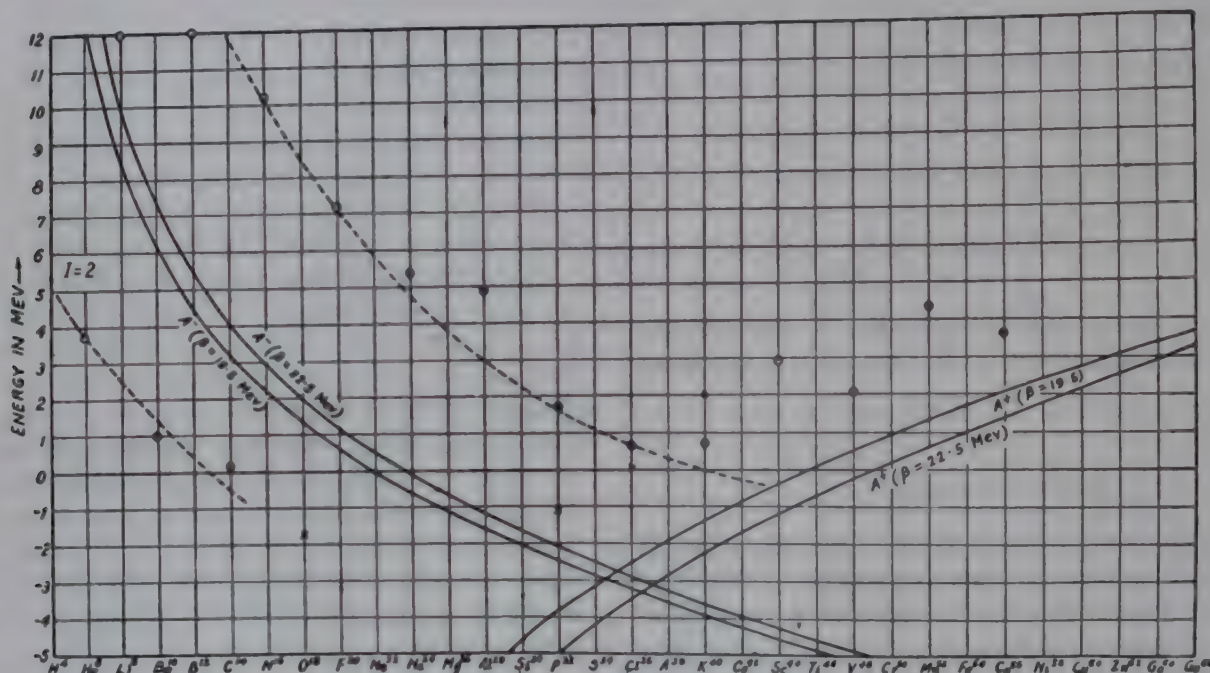


Fig. 3

The energy-release in the case of β^- -active and β^+ -active nuclei generally follows the A^- and A^+ -curves. The ringed points give the actual values, wherever available. On the right-hand side, however, data are generally very uncertain; but whatever is available appears to be in agreement. V^{40} is nearly stable, decaying only by K -capture and having a long life of 600 days. As we proceed outwards the nuclei release progressively larger amounts of energy, and become short-lived. When E is large, intermediate levels are formed and the energy-release takes place through β -rays and γ -rays emitted in cascade. As mentioned earlier, the data on such cases have to be carefully sifted, and most are yet uncertain.

When I is even, we can place the nuclei in two categories:

1. *Even-even nuclei* (N even, Z even). For such nuclei we have

$$E^- = A^- + \chi(Z+1, A) < A^-,$$

$$E^+ = A^+ + \chi(Z-1, A) < A^+ \quad \dots (5)$$

for $\chi(Z, A)=0$, when Z, N are both even, and $\chi(Z, A)$ is uniformly negative when Z and N are both odd. Hence Z being even here $\chi(Z+1, A) < 0$.

The A^- - and A^+ -curves have been drawn for two values of β , namely, 19.5 and 22.5 Mev. The first is Bethe's value, the second is a trial value. The ringed points give us the observed values of energy-release. It shows that $\chi(Z, A)$ is negative whenever Z is odd and is of the order of 3-5 Mev. The dotted curve has been drawn for β^- -emitting nuclei with Z odd. For even-even nuclei, such a curve would be parallel to the A^- -curve, but according to (5), as much below it, roughly, as the odd-odd nuclei values are above. Only a section of it passing through the points He^6 , Be^{10} and C^{14} is shown. Here the $|\chi(Z, A)|$ terms are smaller than $|A^-|$, which is large on account of small values of M , the mass number, and hence the nuclei are negatron-emitting, though both Z and N are even; but the value of E^- is far smaller than those of contiguous odd-odd nuclei like B^{12} or N^{16} , where the two terms are additive. The curves give a rough indication as to the value of energy-release in a β^- -emission. From O^{18} the A^- -values become smaller as the atomic mass is large, though χ 's continue to be of the same order and all even-even nuclei have E^- negative and therefore the nuclei are stable.

On the right-hand side, the ringed dots show the energy-release wherever known. The stability of even-even nuclei up to Ni^{58} is easily explained. The next even-even nuclei like Zn^{62} or Ge^{66} will prove to be either stable or decaying by K -capture with a long life.

Cl^{36} and K^{40} , which are in the middle of the group, are especially interesting. Cl^{36} , like Cu^{64} , has been found (Grahame and Walke⁶) to decay both by β^- -emission to A^{36} as well as by K -capture to S^{36} . K^{40} , which occurs naturally, is similar, as it decays by negatron emission to Ca^{40} and by K -capture, but probably also by positron emission to A^{40} , as several investigators have found, but its spectrum requires re-investigation. Positron emission by K^{40} is indicated by the annihilation radiation of 0.5 Mev., found by Klemperer.

It has been found for other groups that all nuclei which decay by simultaneous emission of negatrons on one hand, and positrons or K -capture on the other hand, like Cu^{64} , occur round about the points where the A^- -curves cut the A^+ -curves.

So far, we have examined the data available for nuclei belonging to the groups $I = -1$ to $I = 6$, and in more recent work by A. K. Saha and S. Ghosal, the method has been extended from $I = 7$ to $I = 20$. We have generally confirmed that the stability of nuclei, and the energetics of β -emissions, can be explained in the same general way; but it is not so easy to deal with level-formations in the nucleus. Probably the agreement will be far better when a more accurate mass-defect formula for even-even stable nuclei is available. A few important deductions arising out of the present investigation may be noted.

(a) Li^5 is expected to be a nucleus having a long life of several years, and decaying by K -capture to He^5 , which should be stable.

(b) A^{39} , reported as a β^- -nucleus with a life of 4 min., is a glaring anomaly: A^{39} is expected to be a long-lived nucleus decaying by K -capture to K^{39} .

(c) Even-even nuclei may not always be stable, if the nucleus is a bit off the main line of stability. Thus Ti^{44} , Cr^{48} , etc., if they could be prepared, they would be found,

like C^{14} , to be long-lived products, decaying in these cases by K -capture.

(d) It is probable that Ca^{48} , stated by Nier to be a rare stable isotope of calcium with a frequency of 0.2 per cent, is illusory, like Co^{57} , which was once believed to be stable, but was predicted by us to be unstable. This prediction has been confirmed; recently I. Curie⁷ has independently come to the view that a stable Ca^{48} does not exist. This nucleus, and Ti^{52} , Cr^{56} , Fe^{60} , if they could be made, would be found unstable, decaying like C^{14} with the emission of slow β^- -rays. The first stable nucleus in the group $I = 4$ should be Ni^{64} .

(e) The radioactive nuclei V^{50} , Mn^{54} , Co^{58} should decay with both β^+ and β^- -emissions and K -capture, but only β^+ -emission and K -capture activity have been reported so far. If they are found not to emit β^- -rays a fundamental difficulty arises in the theory of β -emission.

(f) The spin-dependent part of the nuclear binding energy, namely, $\chi(Z, A)$ is found generally to be of the order of a few million electron volts, while according to classical theory it should be $\simeq \frac{Zev}{cr^2} \mu_k$, where Z is number of charges in the nucleus, v is the velocity of a nucleon inside in the nucleus, and μ_k is the nuclear magnetic moment. Making plausible assumptions about these quantities, we find that $\chi(Z, A)$ is of the order of about 10-20 kilovolts. This shows that we have to apply some type of meson theory to find out the right order of value of the spin-dependent part of the nuclear binding energy. Actually, D. Bose has deduced the right order of value for $\chi(Z, A)$ using the vector meson theory of Kemmer, but as theories of meson field as Louis de Broglie has said, are not yet definitive, this point has not been pursued further.

¹ Seaborg, *Rev. Mod. Phys.*, **16**, 1 (1944).

² Saha, Sarkar and Mukherjee, *Proc. Nat. Inst. Sci. India*, **6**, 45 (1940).

³ Kruger and Ogle, *Phys. Rev.*, **67**, 273 (1945).

⁴ Maier-Leibnitz, *Z. Phys.*, **122**, 233 (1944).

⁵ Giebert, Roggen, Rossel, *Helv. Phys. Acta*, **17**, 97 (1944).

⁶ Grahame and Walke, *Phys. Rev.*, **60**, 909 (1941).

⁷ Curie, *J. Phys.*, (8), **6**, 209 (1945).

79. CONDITIONS OF ESCAPE OF RADIO-FREQUENCY ENERGY FROM THE SUN AND THE STARS

(*Nature*, **158**, 549, 1946)

In several communications in *Nature*^{1,2,3,4} and elsewhere, various British, Australian and New Zealand workers have described experiments carried out during the War which prove conclusively that during times of solar disturbance there are large outbursts of radio-frequency energy from the sun. The wave-lengths measured vary from 1.5 metres to 30 metres (10 Mc. to 200 Mc.). On a rough estimate, the intensity of emission appears to be, as Appleton¹ has shown, 10^4 times the value calculated from the black-body formula taking $T=6,000^\circ\text{K}$. If we assume that the radiation proceeds only from the active areas, as appears to be corroborated by the experiments now in progress at the Cavendish Laboratory, Cambridge³, the emissivity of these regions for the range mentioned is increased nearly 10^7 - 10^8 times the blackbody radiation.

There are certain difficulties in the escape of these radiations from the sun to which attention may be directed. It has been found that the quiescent sun has, like the earth, a magnetic field of the order of 50 gauss, but the spots show a field of much higher range, from 100 gauss in the case of tiny spots to 4,000 gauss for the largest ones⁵. If the radio waves are generated anywhere within the outer layers of the sun, then they must follow the physical laws of electro-magnetism. According to the magneto-ionic theory of Appleton, an electromagnetic wave of frequency f , generated anywhere on the earth's surface, can escape vertically from the earth only when the frequency of the waves exceeds certain limits, depending upon the maximum electron concentration above. The exact mathematical relations are

$$f_0^2 > \frac{4\pi N e^2}{m} > 8.0 \times 10^7 \cdot N.$$

$$f_e(f_e + f_h) > \frac{4\pi N e^2}{m} > 8.0 \times 10^7 \cdot N.$$

Here N is maximum number of electrons per c.c. in the ionosphere, f_o is frequency of the o -wave, f_e is frequency of the two extraordinary waves, f_h the characteristic gyro-frequency of the electrons under the total field H , $f_h = eH/4\pi \text{ cm.} = 1.32 H \text{ Mc.}$ These conditions set a lower limit to the frequency of the radiations which can escape from the earth, and their validity has been verified by innumerable experiments.

If we apply these conditions to the sun, and also to the stars, we find at once that severe physical conditions have

to be imposed on the emission of radio-waves from these bodies. Taking first the o -wave, we should have

$$N < 1.25 \times 10^{-8} \cdot f^2$$

$$< 1.25 \times 10^8 \text{ for } f = 10 \text{ Mc.}$$

$$< 5 \times 10^2 \text{ for } f = 200 \text{ Mc.}$$

The concentration of electrons in the different layers of the sun has been found by well-tried astrophysical methods⁶ to have the mean values of 10^{13} per c.c. for the reversing layer, 4×10^{11} per c.c. for the mean chromosphere, and 4×10^8 per c.c. for the base of the inner corona. It is, therefore, obvious that o -radiations of radio-frequency range which we obtain from the sun cannot have their origin either in the reversing layer or the chromosphere, but only in the corona, and that also progressively in the outer layers as the wave-length is increased. But the corona has been shown to be a purely 'electron atmosphere' without any heavier atomic particles, excepting very small concentrations of heavily ionized Fe, Ni and Ca, which produce the coronal lines. The mechanism of origin contemplated by Greenstein, Henyey and Keenan⁷ which ascribes the radio-waves to recombination between protons and electrons therefore appears to fall to the ground in the case of the sun.

The e-waves. For the e -waves, the value of f_h is decisive, and this varies from 66 Mc. for the quiescent sun to roughly 4,000 Mc. for the spot, taking $H=3,000$. These are frequencies of an order which are not contemplated in Appleton's theory, but a little work shows that whatever has been said regarding the o -wave also applies to *that* e -wave which corresponds to the condition $f_o (f_o - f_h) > 8 \cdot 10^7 \times N$ with greater emphasis. In fact, this wave cannot escape unless f_o has very high values, $> 66 \text{ Mc.}$ The e -wave corresponds to the condition $f_o (f_o + f_h) > 8 \times 10^7 N$.

The possibility of reception of this wave on the earth has generally been ignored by European and American workers, but it has been obtained distinctly on several occasions by Toshniwal⁸ at Allahabad, and his findings have been confirmed by Leiv Harang⁹. Recently, Saha and B. K. Banerjee¹⁰ have shown that any radio-wave generated on the earth would be decomposed into three waves as in inverse Zeemann effect, the p -component corresponding to the o -wave, and the S -components to the e -waves. If this deduction be accepted, we at once see that for the spots, the e -wave of this type has a far greater probability of

escape; for now we should have

$$N < 1.25 \times 10^8 f_e(f_e + f_h)$$

$$< 1.25 \times 10^8 f_e f_h, \text{ taking } f_h \gg f_e$$

$< 5 \times 10^8$ for 10 Mc. waves, and $< 10^{10}$ for 200 Mc. waves; taking $f_h = 4,000$ Mc., corresponding to the field-strength of 3,000 gauss. For a quiescent sun, the figures are $N < 8 \times 10^6$ and 1.4×10^8 respectively. Hence the probability of escape of these waves from the quiescent sun continues to be very small, if the wave originates in the deeper layers. For larger spots, the field generally increases and has been known to reach values as high as 4,000 gauss.

From these arguments, it is fair to draw the conclusion that the large spots are just the regions whence the e -waves of the frequency range 10-200 Mc. can escape. The value of the fields given above corresponds to the level where the atomic lines originate, but Chapman¹¹ thinks that fields might increase to even 10,000 gauss in the deeper layers. If this be true, the e -waves can originate even from much deeper layers. Further, it is well known that the spot is a region of far lower temperature, and the electron concentration in the spot is much lower than on the general surface of the sun; this circumstance also helps the escape of the e -waves.

If these considerations be on the right line, the radio-waves received on the earth when a big spot is in the centre of the sun's disk should be circularly polarized, and its sense of polarization will be determined by the sign of the field.

These considerations apply equally well to the stars composing the Milky Way region, from which waves in the metre range have been observed³. They cannot be emitted from the surface of the hotter stars, but from cooler stars of G -, K - and M -type, and probably the escape of the radiation is facilitated by the development of spots in these stars, analogous to the case of the sun. The difficulties of the dilution factor pointed out by Greenstein *et al.*⁷ are therefore eased to a large extent, as, according to Dunham¹², the disk area covered by K - and M -stars is nearly 10^4 times that of B -stars.

University College of Science,
Calcutta.
Aug. 30.

¹ Appleton, *Nature*, **156**, 543 (1945).

² Hey, Phillips, Parsons, *Nature*, **157**, 297 (1946).

³ Hey, *Nature*, **157**, 47 (1946).

⁴ Pawsey, Payne-Scott, and McCready, *Nature*, **157**, 158 (1946).

⁵ Nicholson, *Pub. Astro. Soc. Pacific*, **45**, 51 (1933).

⁶ See for reference, Unsöld, "Sternatmosphäre", 82, 436, 440.

⁷ Greenstein, Henyey, Keenan, *Nature*, **157**, 806 (1946).

⁸ Toshniwal, *Nature*, **135**, 471 (1935).

⁹ Harang, *Terr. Mag.*, **41**, 143 (1936).

¹⁰ Saha and Banerjee, *Ind. J. Phys.*, **19**, 159 (1945).

¹¹ Chapman, *Nature*, **124**, 19 (1929).

¹² Dunham, *Proc. Amer. Phil. Soc.*, **81**, 277 (1939).

¹³ I am indebted to Dr. J. A. Ratcliffe for showing me these experiments during my recent visit to Cambridge.

80. ORIGIN OF RADIO-WAVES FROM THE SUN AND THE STARS

(*Nature* **158**, 717, 1946)

It has been shown in a previous communication¹ that radio-waves of metre range cannot escape from the quiescent sun unless they originate in the corona, where the electron concentration falls to 10^6 — 10^8 per c.c. This seems to me to invalidate, at least in the case of the sun, the free free transition theory of the electron in the field of the proton, put forward by Henyey and Keenan² to explain the origin of 1-metre waves from regions of the Milky Way. For the corona is a purely 'electron atmosphere', where H-ions cannot exist in any considerable quantity without violating the laws of physics. Pawsey, Payne-Scott and McCready³ do not consider it likely that these radiations can originate in any atomic or molecular process, but they suggest an origin in gross electrical disturbances, analogous to thunderstorms on the earth. Greenstein, Henyey and Keenan⁴ in a note in *Nature* concede that the 1-metre waves emitted from the sun have probably a different

origin than in the free free transitions of the electron in the field of the proton.

The object of the present note is to point out that the resources of atomic and molecular processes are not exhausted by the failure of the free free transition process. We have still another group of atomic (or rather nuclear) processes, which can give rise to the radio-waves emitted by the sun and the stars; and these processes are actually stimulated by strong magnetic fields of the type which are characteristic of an active sun. This is the process of excitation by a strong magnetic field of the energy-levels of the nuclei of atoms and molecules, which has been so beautifully demonstrated by the works of Rabi and his school, just before the War⁵. A brief description of the process is given here with the view of bringing out its potentiality for the explanation of the extremely interesting phenomenon of emission of radio-waves by stellar bodies.

The nuclei of many atoms, for example, H^1 , Li^7 , N^{14} , Al^{27} , Na^{23} , Mg^{25} (mostly isotopes with odd massnumber, D^2 , Li^6 , B^{10} , N^{10} being exceptions), possess spin, and finite magnetic moment of the order of $eh/4\pi Mc$, the so-called protonic magnetic moment, though actually the proton has a magnetic moment which is 2.7 times higher. In the absence of a magnetic field, the electron-cloud in the outer incomplete shells of the atom or the molecule react on the nucleus, and give rise to hyperfine structure of spectral lines. As a typical and well-investigated case let us take Na^{23} .

This nucleus has been shown to have a spin of $3/2$ and a magnetic moment of $2.515 (eh/4\pi Mc)$ being taken as unit). In the normal state, the outermost $3s$ -electron, which is in the $^2s_{1/2}$ -state, causes a fine-structure of nuclear levels, characterized by the hfs -quantum number $f = |i + j|$, where i is nuclear quantum number, j is inner quantum number of optical level. For normal Na^{23} , $f = |\frac{3}{2} + \frac{1}{2}| = 2, 1$. The energy difference between the two nuclear levels has been very accurately measured by optical methods, and found to have the value 0.0592 cm.^{-1} in frequency units. This has been confirmed independently⁶.

Normal sodium atoms, say those contained in a sodium lamp, will have some nuclei in the state $f=2$, some in $f=1$, and those in the state $f=2$ are expected to emit spontaneously waves corresponding to the energy difference $\Delta\nu = 0.0592 \text{ cm.}^{-1}$, $\lambda = 17.15 \text{ cm.}$, $1,773 \text{ Mc.}$, the balance between the two states being restored by thermal exchange; but normally such transitions will be extremely rare. We can scarcely expect emission of a single quantum from an excited nuclear level in 10^5 years.

But the conditions are entirely changed, as has been shown by Rabi and his co-workers, when the atoms are placed in a strong magnetic field, which is being crossed at right angles by a much smaller, but rapidly varying field, its period being comparable to those of the emitted radiation but not necessarily equal to these. What happens is roughly as follows: under the action of the strong magnetic field, the atom takes up various orientations as in a Stern-Gerlach experiment, the energies of the orientations being as given below (formulae 1 and 2). The varying field causes these orientations to change rapidly, and in this process, radio-frequency waves are emitted. The energy values of the different orientations, however, change considerably with the field, but Rabi has calculated them from an extension of the theory of the Paschen-Back effect. The formulae for Na^{23} are quoted:

Na^{23} : Nuclear spin $i=3/2$, $f=2, 1$.

m =magnetic quantum number

$=2, 1, 0, -1, -2$ for $f=2$

$=1, 0, -1$ for $f=1$.

ν_{2m} =energy in frequency units of a nucleus with $f=2$ having the orientation 'm':

$$= -\frac{\Delta\nu}{8} + g(i) \mu_B H.m + \frac{\Delta\nu}{2} (1 + mx + x^2)^{1/2}. \quad (1)$$

This holds for $m=1, 0, -1$; for $m=2$, the last terms has the value $\frac{\Delta\nu(1+x)}{2}$, for $m=-2$, the value $\frac{\Delta\nu}{2}(1-x)$.

ν_{1m} =energy in frequency units of a nucleus with $f=1$ having the orientation 'm':

$$= -\frac{\Delta\nu}{8} + g(i) \mu_B H.m - \frac{\Delta\nu}{2} (1 + mx + x^2)^{1/2}. \quad (2)$$

μ_B =Bohr-magnetron, $g(i)$ =Lande factor for nuclear magnetism $= \frac{m}{M} \mu_n/i$, where μ_n is the nuclear magnetic moment in terms of $eh/4\pi Mc$ as unit.

$\Delta\nu$ =separation between the two states in the absence of a magnetic field.

The number $x = \frac{\{g(j) - g(i)\} \mu_B H}{h \Delta\nu} = \frac{2\mu_B H}{h \Delta\nu} = \frac{H}{660}$ for Na^{23} .

Curves of ν -values will be found in *Phys. Rev.*, 57, 769.

The transitions fall in two classes. One set, mostly consisting of those corresponding to $\Delta f=0$, gives ν -values which vary from 0 at vanishing fields to the limiting value of $\Delta\nu/4$ for large fields. For a field of 660 gauss, the wavelengths of the lines emitted are grouped round 1.36 metres, whereas for smaller fields, say 100 gauss, they may be as high as 4 metres. When the field is very large, the emission is grouped round $4 \times 17.15 = 68.60 \text{ cm.}$

The second set, mostly consisting of radiations corresponding to $\Delta f=1$, gives ν -values from $\Delta\nu$ to $x\Delta\nu$; these may give rise to centimetre waves; in fact, for $H=10,000$ gauss, the emission is grouped round 1.1 cm.

These relations have indeed not yet been verified in emission, but in some ingenious absorption experiments by Rabi and his co-workers for Na^{23} , Li^6 , Li^7 , Cs^{133} , K^{41} ; but there seems to be no reason why it should not be possible to design emission experiments, for example, by putting a sodium lamp in a strong magnetic field, which is then crossed by a feeble oscillating magnetic field at right angles. Such sodium lamp ought to give out strong radio-waves of both metre and centimetre range. It is desirable to carry out such experiments in view of the prospect which they hold out of throwing light on the all-important question of stimulation of transitions.

What we have said with respect to Na^{23} will also apply to the nuclei H , Li^6 and Li^7 , B^{10} , B^{11} , N^{14} , Na^{23} , Al^{27} , and other nuclei which possess spin and magnetic moment, and therefore when forming part of an atom or molecule can exist in several well-defined quantized states produced by the electron cloud. The details of calculations will, however, widely differ, and cannot be given in this short

communication; but as in the case of Na^{23} , they will give rise to both metre and centimetre waves.

The most important part in the sun and the stars will, however, be played, not by Na, but by hydrogen, because this forms, according to well-verified astrophysical arguments, 95 per cent of total number of atoms in the atmosphere of the sun; in the stars, also, hydrogen forms in the majority of cases more than 90 per cent of the atmosphere. Na was chosen simply to illustrate the phenomenon. In the spots, on account of lower temperature, the hydrides CH, MgH and SiH (and possibly H_2) are formed in great abundance, and their spectra form characteristic features of spots, but the greater proportion remains in the atomic state. For the H-atom, $\Delta\nu$ cannot be obtained from hyperfine structure experiments, but it has been calculated to have the value of $0.0163 \mu_p = 0.0474 \text{ cm.}^{-1}$, $\lambda = 21 \text{ cm.}$, $x = H/500$, and calculation shows that both centimetre and metre waves can be emitted by the H-atom, corresponding to $\Delta f = 0$, $\Delta f = 1$. But in the case of hydrides, N_2 , CN, no experimental data or theoretical calculations are yet available; but it can be surmised that the characteristic radio-frequency waves would be much longer.

In addition to waves arising out of nuclear transitions, the rotational states of the molecules have also been shown by Rabi and his pupils to be capable of radio-frequency transitions in magnetic fields.

We consider next the possibility of nuclear emission of radio-waves of both centimetre and metre range from the sun and the stars. It now appears extremely probable that the radio-waves observed can be emitted only from the sunspots. The spots show in the centre of the umbra large magnetic fields which vary with the size of the spot⁷, and may reach values as high as 4,500 gauss. The direction of the field is axial (that is, perpendicular to the surface of the sun) in the centre of the umbra, but it becomes inclined to the solar radius as we proceed towards the penumbra, and also diminishes in value. The values of the fields are exactly such as will promote the emission

of centimetre and metre waves according to the schemes given above, and the intensity of emission will be large enough if we can postulate the existence of a small cross-field, having frequencies of the same magnitude as those of the radio-waves. It is not improbable from what we know of the physical nature of sunspots that such variable fields do actually exist, and may partly be provided by the fields of the 'ordinary'-waves, and the 'extraordinary'-waves corresponding to the condition $f(f - f_h) > \frac{4\pi N e^2}{m}$ coming from below, which may, however, find it impossible to penetrate the electron barrier above (see ref. 1).

These speculations, though far from being established on a sure basis, are given on account of their promise of being able to throw light on a series of extremely interesting phenomena, the origin of which has so far appeared to be wrapped in mystery; the moment is also opportune because experiments on the subject are being undertaken all over the world. If the speculations are on the right lines, it appears that sunspots would also strongly emit radio-waves of the centimetre range. I am not aware if any such observation has yet been made. Further, the emission of centimetre waves by the stars of the Milky Way probably indicates the development of spots in these stars, which should belong to the *G*, *K* and *M* classes. But no spectroscopic observation in verification of such a hypothesis is known to me, and from the nature of things it appears extremely unlikely that any such observation is possible, unless the spots in these stars possess gigantic proportions.

¹ *Nature*, **158**, 549 (1946).

² Henyey and Keenan, *Astrophys. J.*, **91**, 265 (1940).

³ Pawsey, Payne-Scott and McCready, *Nature*, **157**, 158 (1946).

⁴ Greenstein, Henyey and Keenan, *Nature*, **157**, 806 (1946).

⁵ See, for example, Kusch, Millman and Rabi, "Radio-frequency Spectra of Atoms and Molecules", *Phys. Rev.*, **57**, 765.

⁶ *Phys. Rev.*, **58**, 441.

⁷ Nicholson, *Pub. Astro. Soc. Pacific*, **45**, 51 (1933).

81. MEASUREMENT OF GEOLOGICAL TIME IN INDIA: THE AGE OF ROCKS AND MINERALS

M. N. SAHA AND B. D. NAGCHOWDHURY

(*Trans. Nat. Inst. Sci. Ind.*, **2**, 273, 1947)

ABSTRACT

In this paper, the various physical methods for finding out the age of rocks are reviewed and methods in use in the Palit Laboratory of Physics are described. Plea is made for setting up a committee on the Age of Rocks by the Council of Scientific and Industrial Research.

The age of the Earth, i.e. the time elapsed since the Earth has been created, has formed a favourite subject of speculation for theologians and astrologers. The Jews say that the Earth was created 3,751 years before the Birth of Christ on the day of the autumnal equinox. God is supposed to have commenced the labours of creation on the first Week Day and finished it in six days, and then took rest on the seventh day which according to Jews was Saturday. Archbishop Usher nearly two hundred years ago calculated the date of creation of the Earth from the age of Patriarchs as narrated in the Bible and came to the conclusion that Jehovah finished the labours of creating the Earth 4,400 years before the Birth of Christ. The Hindus had an ampler sense of time-scale. They consider that creation and destruction of the world was a periodic phenomenon, the periods running to as much as $4,320 \times 10^6$ years. Based on these calculations, the Hindu calendars give out that 1,972,949,046 years have elapsed since the present cycle began. But after all, this was probably idle speculation based upon certain magic properties of numbers as they could not find sufficient events or evidence to fill up such enormous epochs of time and filled them with legendary heroes having incredibly long lives. Scientific study into the question of age of rocks started with the discovery of fossils of animals and plants of past ages by William Smith in the 1780's. It is not our intention here to describe the methods by means of which the geologists estimate the time which have elapsed since rocks of a certain type have been formed. The geological methods though rough give correct indications but for more precise work they have been supplanted by physical methods based on the study of radio-activity.

PRACTICAL IMPORTANCE

The physical methods, as applied in geological investigations, are not only of academic and scientific interest,

but have a great bearing on the all-important question of location of valuable metallic and non-metallic economic minerals, as well as on the question of location of underground deposits of oil. Geophysical methods are also used for detecting hidden or deeply buried geological structures such as folds, faults, dykes of heavy basic rocks, etc., by methods of Torsion Balance Survey or Seismic or Magnetic Survey, etc. A general knowledge both of the lithology of rocks and their structure is essential in the prospecting of valuable mineral occurrences. But to the question of the age of rocks, geological methods alone do not always give an unambiguous answer. To take our own example, India with its enormously thick unfossiliferous pre-Cambrian formations offers a rather puzzling problem for geologists. Her geological history appears to have been rather peculiar and different from the other parts of the world. The Deccan Peninsula appears to have been a solid mass of dry land almost through the whole duration of geological time, and has not been subjected to those periodic marine transgressions, e.g. alternate submersion under the sea and subsequent upheaval, which most areas of our Earth have passed through. On the other hand, Northern India has been subjected to numerous such transgressions of the sea and other violent geological changes. Some parts of the Deccan, as for example, the tract measuring about 200,000 square miles between Bombay and Nagpur, has been flooded by lava flows, thousands of feet in thickness, that have completely obliterated the previous land-surface and all traces of plant or animal life then existing.

Indian geologists have therefore to coin a peculiar nomenclature to designate the totally unfossiliferous rock-systems found in Peninsular India. For instance, the great thickness of sedimentary strata, designated as the *Purana* Group, contains the *Cuddappah* and *Vindhya* systems, while the overlying zone of strata, designated as the *Dravidian* Group, comprises a few fossiliferous systems of Cambrian and younger ages. A vast thickness of land deposits, composed

GEOLOGICAL AGE CORRELATION TABLE FOR INDIA

GEOLOGIC ERA	GEOLOGIC SYSTEM	MAX. STRATA THICKNESS IN THOUSAND FT.	INDIAN FORMATIONS				APPROX. AGE IN MILLION YEARS	DISTINCTIVE OR TYPICAL LIFE	TYPICAL FORMATIONS
			PENINSULA	HIMALAYA	SALT RANGE	OTHER AREAS			
KAINOZOIC	Holocene (Recent)		New raised Beaches & Coral Banks	Dry Deltas & recent River Deposits	Blown sand and loess		0.025	Modern man	
	Pleistocene (Glacial)	4	Nurbuda alluvium, Porbander Sand-stone	Glacial moraine of Kashmir, Sutlej Deposits	Loess Deposits	Indo-Gangetic Alluvium	1	Paleolithic man Pithecanthropus Javaman etc.	
	Pliocene	13	Peninsular Laterite	Upper Siwalik	Siwalik	Irawaddy system Manchar system of Sind	15	Modern Mammals Rhinoceros, Apes, Mastodons, etc.	Formation of the Indo-Gangetic Plains
	Miocene	21	Iron ore deposits of Baripada in Mayurbhanj	Kasauli series	Middle Siwalik	Surma Valley	35	Early Mammals and early Flowering Plants	Himalayan Elevation
	Oligocene	15	Dwarka beds by Kathar	Intrusive granite core of Himalayas	Upper Murree (Eastern part)	Lower Pegu	50		
	Eocene	14	Laki series of Bikaner	Indus, Jammu, Kohat & Ranikot series	Ranikot series	Intrusive granite of Baluchistan	70		
MESOZOIC	Cretaceous	64	Deccan Trap	Plutonic Volcanic rocks of Sikkim	Trans. Indus Salt Range	Cretaceous series of Assam & Intrusive Granites of Burma	120	Reptiles (Saurians)	Extensive lava flows covering a large part of the Peninsula
	Jurassic	20	Upper Gondwana series & Rajmahal Tracts	Tals of Garhwal, Banihal in Kashmir	Jurassic Trans. Indus Salt Range	Lime stones of Baluchistan	150		
	Triassic	25	Middle Gondwana & Mahadev Series	Trias sandstone of Central Himalayas		Napeng beds of Burma	190	Amphibians	Limestone & Sand Stone of Baluchistan & Central Himalayas

GEOLOGICAL AGE CORRELATION TABLE FOR INDIA—Continued

GEOLOGIC ERA	GEOLOGIC SYSTEM	MAX. STRATA THICKNESS IN THOUSAND FT.	INDIAN FORMATIONS				APPROX. AGE IN MILLION YEARS	DISTINCTIVE OR TYPICAL LIFE	TYPICAL FORMATIONS
			PENINSULA	HIMALAYA	SALT RANGE	OTHER AREAS			
Paleozoic	Permian	13	Lower Gondwana Ranigunj-Barakar system	Shale & Limestone of Central Himalayas	Limestone of Salt Range	Limestone of Shan States	220	Amphibians Plants, Fossils, (Ferns etc.)	Formation of Gondwana Coal seams and the recession of the Sea
	Carboniferous	40	Talchir, Lower Gondwana coal measures	Pir Panjals		Subansiri Beds of Assam	280 320	Early fishes and first Vertebrates	
	Devonian	37		Chitral series of N.W.F.P.					
	Silurian	15		Spiti Valley in Kangra of Kashmir		Shales & Limestone of Northern Shan States	350 400	Gastropods Crustacea Cephalopods and other Invertebrates	Vindhyan elevation movements
	Ordovician	40		Kashmir Ordovician					
Archaean	Cambrian	40	Upper Vindhyan (?)	Haimanta System of Central Himalayas	Cambrian of Salt-range (?)		500	Corals and Low forms of Marine fossils, like Trilobites etc.	Cuddappah formation and extensive earth movements
	Proterozoic	Thickness very great actual figures unknown	Dharwar and Lower Vindhyan (?) system			Shillong system	800	Very early forms of life rarely found	Dharwar and Aravalli formations (oldest sedimentary formations)
	Archezoic Eozoic		Chotanagpur Gneiss			Fundamental Intrusive Granites of Burma, Assam and Baluchistan	No estimation usually surmised upto 1750	Very Rare or No Fossil Remains	Fundamental Gneiss and Intrusive Granites of Assam, Chotanagpur & Burma

←— ORIGIN OF EARTH ABOUT 2000 MILLION YEARS —→

Fig. 1

of river-borne sediments, which carry our principal coal deposits, has been designated as the *Gondwana* system and so on. These have been correlated, on such evidence as is available on purely lithological grounds, to the standard systems of the European geological scale. A vast system of crystalline metamorphic rocks, known as the *Dharwar* system, has been assigned to the *Archean* age, while the upper *Vindhyan* system, formerly classified as *Purana*, is now with some justification correlated to the Cambrian. But most of these assignments, in the absence of reliable fossil evidence, lack solid confirmation; and accurate correlation with well-established systems has still to be worked out by other means. In the great extra-Peninsular mountain-zone which bounds Deccan to the west, north and north-east, we stand on quite different ground. Here, wherever fossil evidence is found in the various rock formations, it has enabled a more or less precise correlation to be established with the accepted standard systems of European and American geology. But here also, when fossil evidence is lacking or obscure, the same uncertainty occurs. A striking example of this is the recent controversy regarding the age of the Salt-series in the Salt Range mountains of the Punjab. This important mountain range lies in the Doab between the Jhelum and the Indus and carries rock-salt deposits of considerable magnitude that has supported important salt mines for centuries. One school of geologists holds this formation to be of the Cambrian age, while another school, on equally plausible grounds, hold them to be of the Tertiary age. This controversy has lasted for nearly five decades. The Cambrian system of rocks is held to be nearly 500 million years old, while the oldest Tertiary system is not more than 50 million years. To the non-geologists, these widely divergent views seem anomalous. Recently, Professor Birbal Sahni of the Lucknow University, by using a new technique, has detected minute plant fossils *in situ* in the saline-series, which go to prove a lower Tertiary age for the series. The *in situ* nature of these fossils (which are microscopic in size) is doubted by the Geological Survey of India and geologists of various Oil Companies. (*Nature*, 1944, p. 462, Vol. 153; *Nature*, 1945, p. 258, Vol. 155).

MODERN TECHNIQUE OF GEOLOGICAL AGE DETERMINATION IN THE U.S.A.

A somewhat similar condition prevailed in the U.S.A. Systems of rocks lacking in indubitable fossil testimony were found difficult to correlate with those of Europe, and names such as *Mississippian*, *Pennsylvanian* and *Laurentian* have been coined by American geologists. In order to collect more precise scientific evidence regarding the age of rocks in the U.S.A., a National Committee under the Chairmanship of Dr. A. C. Lane, Professor of Geology in the Harvard University, was set up by the National

Research Council of the U.S.A. in 1932. The work of the Committee has resulted in the development of more accurate physical methods in the age determination of rocks and minerals, employing the mass-spectrograph, the interference spectroscope, determination of radio-activity by electronic methods, lead-helium ratio, micro-volume measurements, etc. Such geophysical methods have not yet been used in India, except some stray measurements by N. C. Nag, Swaminathan, Mahadevan, Dube and one or two others.

The Time Scale of Geology.—The time scale of the geologists is derived by painstaking study of the surface rock formations. The fossil remains of past epochs that get embedded in sedimentary rocks are the hour-marks on the face of his geologic clock, for fossil remains have been found to show the successive stages of evolutionary development through the ages. There are, moreover, periods of prolific development of particular species over a large part of the face of the Earth during certain geologic eras. The Carboniferous era of geologists, so called because of the sudden development of types of conifers and other exuberant vegetation over large tracts of the world's surface, is the time during which the principal coal-seams of the world were formed. Limestones and chalk are also attributed to a sudden proliferation of several species of small foraminifera, corals, crustacea and shell-like creatures. The oldest fossil remains are attributed to the Cambrian age. The actual time elapsed since the Cambrian age cannot be estimated accurately, but it is supposed to be somewhere about 500 million years. Geologists have estimated the duration of an epoch by the thickness of the sedimentary layers corresponding to that epoch and by other means. The estimates vary greatly as the thickness of sedimentary deposits of the same epoch are not of equal thickness, nor is the rate of deposition of sediment anywhere near constant.

Pre-Cambrian Age.—All rocks older than the Cambrian age, that is, all rocks formed before the advent of life on the globe, are lumped together into one group usually called 'Archaen' meaning old or pre-Cambrian. The Archaen rocks according to current estimates of geologists cover a period of time nearly four to six times as long as the total time from the Cambrian rocks down to the present time. Since there are no fossil remains in these old rocks it is difficult to attach much importance to the estimation of age of these old formations. There are also frequent cases when the fossil remains in a particular rock are entirely unsatisfactory and cannot be used to determine the era to one's satisfaction. There are other cases where an independent check may be desired due to conflict of evidence. In addition, the question of absolute age of rocks on geological evidence alone will ever remain unsatisfactorily answered in all parts of the world.

Physical Methods.—Physicists have long attempted to

find a solution to this vexed problem in terms of a physical process whose time rate of variation can be correctly determined. One of the earliest attempts was by Lord Kelvin who tried to calculate the age of the Earth from its rate of cooling. He assumed that the Earth was originally at the temperature of the surface of the sun, i.e. about 6000°C ., and that it has cooled down through the ages at a uniform rate depending on the internal and surface temperatures. He calculated the thermal conductivity of the Earth from several samples of rock and obtained a mean value. The results that he obtained were, however, unacceptable to the geologists as they were very much lower than the estimates of geologists. In fact his estimate of a few lacs of years were not even enough to account for the long span of evolution of life on Earth. This contradiction proved fatal to the conductivity method of measuring ages and showed that Kelvin had neglected some very important factor.

Radio-activity.—The discovery of Radio-activity of Uranium and Thorium late in the nineteenth century brought this factor to light and gave a veritable physical time-clock for estimating ages of rocks. As is well known, a few heavy atoms like uranium, thorium and actinium atoms are found to disintegrate at a constant rate breaking up into simpler atoms. This rate is a characteristic of the type of disintegrating heavy atoms and is entirely unaffected by temperature, pressure or the state of chemical combination of the radio-active element. Uranium for example breaks up by emitting successively eight doubly charged helium atoms or α -particles and ends up finally as lead of isotopic weight 206 ($\text{Pb } 206$). The rate of disintegration is expressed in half-lives which simply means the time in which half of the total number of radio-active atoms of a particular element will disintegrate. Uranium which is at the head of the uranium-series of disintegrations has a half-life of 4,400 million years. The successive elements of the uranium series disintegrate very much faster and do not have any geological significance due to the shortness of their lives. Radium is the longest lived of the daughter elements of uranium and has a half-life of 1,600 years which is quite small compared to the duration of the geological epochs.

Thorium behaves very similarly to uranium giving rise to another chain of disintegrations of which again thorium has the largest half-life of 18,000 million years. The final end product in this case is also an isotope of lead of isotopic weight 208.

The third chain of disintegration, the actinium series can now preferably be called the Actino-uranium series, since the parent of the actinium series is not actinium but an isotope of uranium of mass 235 whose half-life has been recently estimated by Nier at 700 million years. Uranium of the mass 235 is present in a ratio of 1:139 with the ordinary uranium isotope of mass 238 and disintegrates

finally to lead 207. All these three radio-active elements can be used as geological time-clocks as their rates of disintegrations are known.

Besides the isotopes 206, 207 and 208, lead contains another isotope of mass number 204 in very small proportion which appears to be unconnected with any radio-active disintegration, though the opinion has been expressed that it may be the result of α -ray disintegration of $\text{Pb } 208$ followed by two successive β -ray disintegrations. But this theory has not been proved, and we may take $\text{Pb } 201$ as a stable isotope, unconnected with any radio-active process.

When lead is found to occur in a rock, either containing radio-active matter like U, or Th, or entirely free from these, the first task is to estimate accurately the proportion of uranium, lead and thorium. This is a comparatively easy task in analytical chemistry. The second task will be to estimate the chemical weight of lead. This has been found to vary widely from 206 to 208, the first figure being found in rocks containing high proportion of U, e.g. in Curite, Uraninite, the last in rocks containing high proportion of Th, e.g. in Thorianite, but in rocks containing no *radio-active matter*, the atomic weight of lead is generally found to be 207.23. What is the cause of this wide variation in the atomic weight of lead?

It is obvious that in the rocks where the atomic weight of its lead is about 208, e.g. in Thorianite from Ceylon, most of the lead has been derived from the disintegration of thorium and in those minerals where the atomic weight is nearly 206, e.g. the Curite from Katanga in Belgian Congo, it is derived mostly from the disintegration of uranium. But such rocks are few and in most minerals the atomic weight varies all the way between 206 and 208. To explain these wide variations we may start with the plausible assumption that when rocks were formed, they not only contained $\text{U } 238$, $\text{U } 235$, $\text{Th } 232$ in different proportions, but also contained some lead from the primeval matter. After the rock has aged sufficiently additional amounts of lead were formed from the decomposition of U and Th and were added to the lead already present, thus changing its atomic weight, and the relative proportions of the different isotopes of lead. We can generally take that the lead in a rock is composed of two types of lead: (i) non-radiogenic lead which was deposited in the rock from the primeval matter when the rock was formed, and (ii) radiogenic lead, which grew subsequently out of the disintegration of uranium and thorium.

To test this hypothesis, our next task is to estimate the proportions of the different isotopes in this non-radiogenic and the radiogenic lead. The isotopes cannot be separated chemically, but complete separation by physical methods have been devised lately (method of thermal diffusion). Here we are concerned only with the estimation of relative proportions of the isotopes, and this can be done either (1) by the method of hyperfine structure analysis or (2)

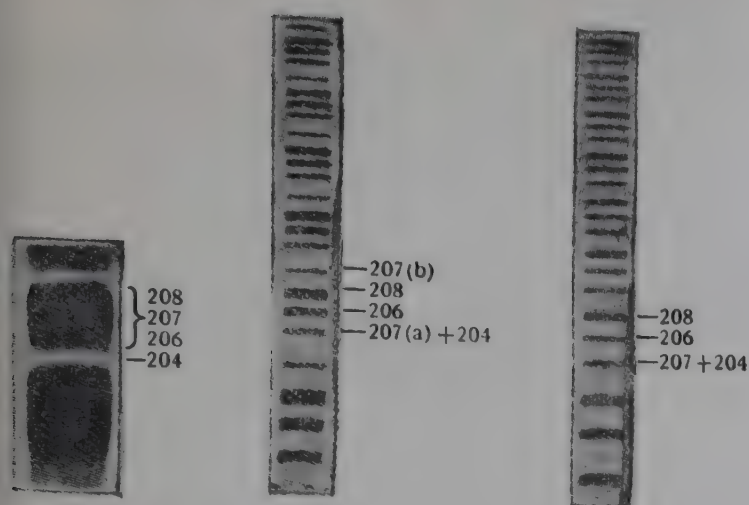


Fig. 2

by the mass-spectrograph; the first method depends on the fact that spectral lines due to the four isotopes slightly differ in wavelength and structure and if apparatus of extremely high dispersion be used, they can be separated.

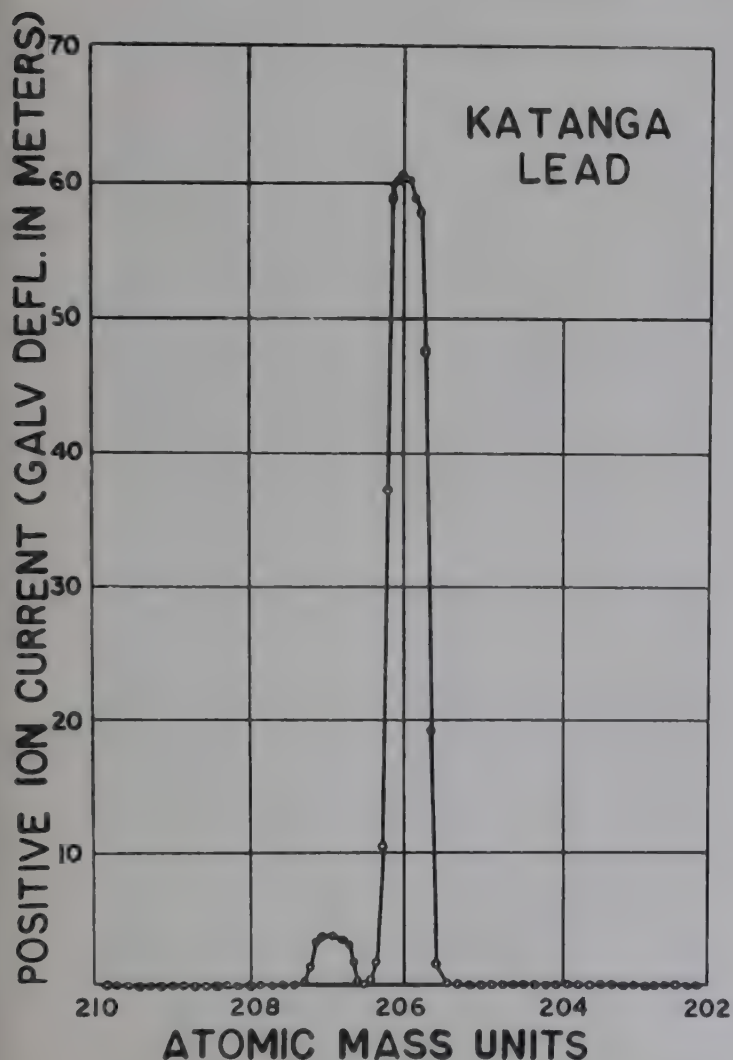


Fig. 3

The relative intensities of the components ascribed to the isotopes give us their relative proportions.

The mass-spectrograph is, however, a far more powerful and accurate apparatus for this purpose, and in the hands of Nier and others, it has received so many improvements that relative proportions of the isotopes in a sample can be estimated quickly and quite accurately.

Nier and others have analysed isotopic ratios in different samples of lead with the help of the mass-spectrograph from rocks and minerals completely free from radio-activity. They find that in the main, the isotope ratios for non-radiogenic lead is fairly constant and their average values are: (Nier: P.R. 55, 194)

Pb ²⁰¹	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸
1	18.8	15.7	38.9

with the mean atomic weight as 207.23. There are, however, slight differences in isotope ratios from sample to sample quite outside the range of error claimed by Nier. These variations are slight and, for practical purposes of age determination, can be neglected. For more complete analyses the extreme values of isotope ratios should be taken into account.

One can picture that the primeval magma out of which the rocks have been formed contains lead in which the isotopes are in the constant proportion approximately given by Nier's analysis. Supposing a rock in some distant geological epoch has trapped in it radio-active elements together with the primeval lead. Through the ages the radio-active elements will now disintegrate to give certain isotopes of lead. The proportions of these isotopes in lead will then increase while lead isotope (204) will remain the same and if the original proportion is assumed as given above the amount of increase of each lead isotope can easily be estimated.

The following table (fig. 4) gives an idea of the proportion of isotopes of lead occurring in some of the representative minerals of North America. Three selected non-radiogenic lead minerals are also analysed for comparison and to show the natural range of variation of the proportions of the isotopes. It is clear from these figures that the total percentage of lead in a mineral alone is no indication of the age of the mineral. Colorado Pitchblende and the Connecticut Samarskite contain the same percentage of lead although it is obvious from the isotope analysis that the Pitchblende contains about six times the quantity of non-radiogenic lead compared to the Samarskite. An exact analysis yields an age of about 50×10^6 years for the Pitchblende compared to 280×10^6 years for the Samarskite.

Geologists and geochemists like Keevil and Urry have used a rough modification of this method which avoids the complicated and difficult isotope ratio analysis of lead.

PHYSICAL & CHEMICAL ANALYSIS OF TYPICAL MINERALS

NAME	CLASS	LOCATION	%U	%Th	%Pb	Pb ²⁰⁸	Pb ²⁰⁷	Pb ²⁰⁶	Pb ²⁰⁴	MEAN At wt
1. URANINITE	URANEUS MINERALS	PARRY SOUND, CANADA	6.9	2.9	10.8	1.52	7.40	100	.006	
2. PITCHBLEND		WOODS MINE, COLORADO	72.3	.11	.314	38.0	19.4	100	1.01	
3. CURITE		KATANGA, BELG. CONGO	65	.04	.96	.178	6.18	100	×	
4. MONAZITE	THOREOUS MINERALS	HURON CLAIM, CANADA	.28	15.6	1.5	100	2.11	11.6	.011	
5. MONAZITE		LASVEGAS, NEW MEXICO	.12	9.39	.372	100	1.25	10.1	.028	
6. THUCHOLITE	MIXED MINERALS	PARRY SOUND, CANADA	4.63	.90	.187	6.9	5.88	100	.024	
7. SAMARSKITE		GLASTONBURY, CONNECTICUT	6.9	3.1	.314	21.3	7.6	100	.167	
8. GALENA	NON-RADIOGENIC LEAD MINERALS	DURANGO, MEXICO	NIL	NIL	×	38.5	15.7	18.7	1.00	207.227
9. GALENA		FRANKLIN, NEW JERSEY	NIL	NIL	×	36.5	15.5	17.2	1.00	207.233
10. GALENA		TETREAUULT, CANADA	NIL	NIL	×	35.6	15.2	16.3	1.00	207.239

Fig. 4

There are a number of well-known uranium and thorium minerals which normally occur with little lead, e.g. Uraninite, Curite, Gumite, etc. Geochemists make the plausible assumption that all the lead occurring in these minerals is wholly of radiogenic origin. The chemically determined proportion of lead in the mineral is then determined and attributed wholly to the disintegration of uranium or thorium or both as determined from the radio-active content of the mineral. The expression which is used is

$$T \text{ (in million years)} = \frac{7,600 \times \text{Lead (gms.)}}{U + .36 \text{ Th}}$$

and is applicable for minerals of less than 500 million years without appreciable error. It must be emphasised, however, that the result, although sometimes quite concordant with the earlier and more rigorous method of isotopic analysis, is at other times in grievous error. We cite as an example the Curite from Belgian Congo which yields an age of 125 million years by this method yields an age of 115 million years by the more accurate analysis of the lead isotopes. The results are quite concordant. In the case of the Connecticut Samarskite obtained in a very good condition, the same method yields a value of 380 million years which is somewhat in excess of the value of 250 to 280 million years obtained by isotopic analysis methods. This excessive value is due to the presence of a small amount of non-radiogenic lead in the mineral. Larger amounts of non-radiogenic lead in the mineral might give even larger discrepancies.

Estimation of Uranium and Thorium.—The estimation of relative proportions of Th and U is a very important task in all these problems. So far they have been estimated by chemical methods alone which are rather tedious and time-exhausting. Recently physical methods for quick estimation of thorium and uranium have been evolved. They depend on the radio-active properties of these elements.

These three methods may be tabulated as:—

- (1) Method of Finney and Evans by α -counting.
- (2) Method of β -ray ionisation chamber and foils.
- (3) Method of β -ray counters and foils.

	Uranium Content	Thorium Content	References
Method of Finney and Evans	20.08 $\pm$ 1.42%	60.94 $\pm$ 2.2%	Nag, Das and Das Gupta, <i>Proc. Nat. Inst. Sc.</i>
β -ionisation method	21.16 $\pm$ 1.1%	60.24 $\pm$ 2.0%	Mousuf (in preparation for press), M.Sc. thesis, 1944.
β -Counter method	20.5 $\pm$ 1.7%	61.3 $\pm$ 2.5%	Nag (private communication).
Chemical Analysis	21%	61%	P. B. Sarkar, <i>Science and Culture, Bull. Nat. Res. Council.</i>

These methods are all essentially the same in principle and the results of a sample of Thorianite measured by the three different methods are compared here with the results of direct chemical analysis. The Thorianite was a gift from Prof. D. N. Wadia, for some time Geological Adviser to the Government of Ceylon.

Within the errors involved in the experiment all the methods give approximately the same result and are about equally reliable. The β -ray ionisation current method which has been developed in the Palit Laboratory gives the quickest and simplest quantitative analysis of all the methods including chemical analysis but is applicable only for quantities of radio-active elements of 1 per cent or greater in the mineral. It is now in use as a standard method for finding proportions of uranium and thorium in minerals regularly in this laboratory. The chemical method suffers from the defect that losses on ignition may be large where small amounts of U or Th is involved. The method of Finney and Evans has been very extensively used and consists in counting the alpha particles emitted from a

given sample and noting the number of counts with various thicknesses of thin absorbing foils. This method is limited by the difficulties of counting kicks of a galvanometer over long periods of time and the impossibility of counting more than 100 per second. If the radio-active contents of a mineral sample is large, i.e. greater than 20 per cent of the total weight of the mineral, large errors may be introduced.

The Lead 206/Lead 207 Ratio Method.—Nier has recently proposed an ingenious method which does away with measurements of uranium and thorium content as well as the chemical estimation of lead in the mineral. He determines the isotope ratio of the lead by the mass-spectrographic method and calculates the geological age from these data alone. Uranium has two isotopes, U^{235} and U^{238} , both of which disintegrate finally to lead but to two different isotopes, 207 and 206, and at two different rates. The half-life U^{235} is 700 million years and this isotope thus disintegrates at a rate nearly four times faster than U^{238} . Suppose initially both the uranums start to disintegrate and no lead is present in the mineral, then Pb^{207} will accumulate at a rate nearly four times as fast as Pb^{206} . The isotope ratio of Pb^{207}/Pb^{206} will increase with the age of the mineral. This straight forward idea has to be modified to take three factors into account. Firstly, the initial quantities of U^{235} and U^{238} or their ratio has to be known. Their present ratio has been measured accurately from various sources and yields a more or less constant ratio of $U^{235}/U^{238}=1/139$. Knowing their rates of disintegration the ratio at any geological time can be calculated very simply. Secondly, the mineral may contain an unknown quantity of non-radiogenic lead. The lead 204 isotope is then used as an index of the presence of non-radiogenic lead and corrections are made in the lead (206/207) ratio by subtracting a certain fraction of lead 206 and 207 isotopes from the respective quantities to eliminate the effect of non-radiogenic lead. For example, take the Pitchblende from Colorado in our table, the apparent Pb^{207}/Pb^{206} ratio=19.4/100, but since Pb^{204} occurs, non-radiogenic lead is present in the sample. The average ratios of isotopes in non-radiogenic lead have been given earlier and are subtracted from the lead ratios of the lead from Pitchblende,

207	206	204
19.4	100	1.01
15.84	18.98	1.01
3.6	81	

and the ratio of Pb^{207}/Pb^{206} to be used is 3.6/81. Thirdly, corrections have to be made to take into account the fact that the U^{235} is being depleted much faster than U^{238} and hence, even though the rate of disintegration of U^{235}

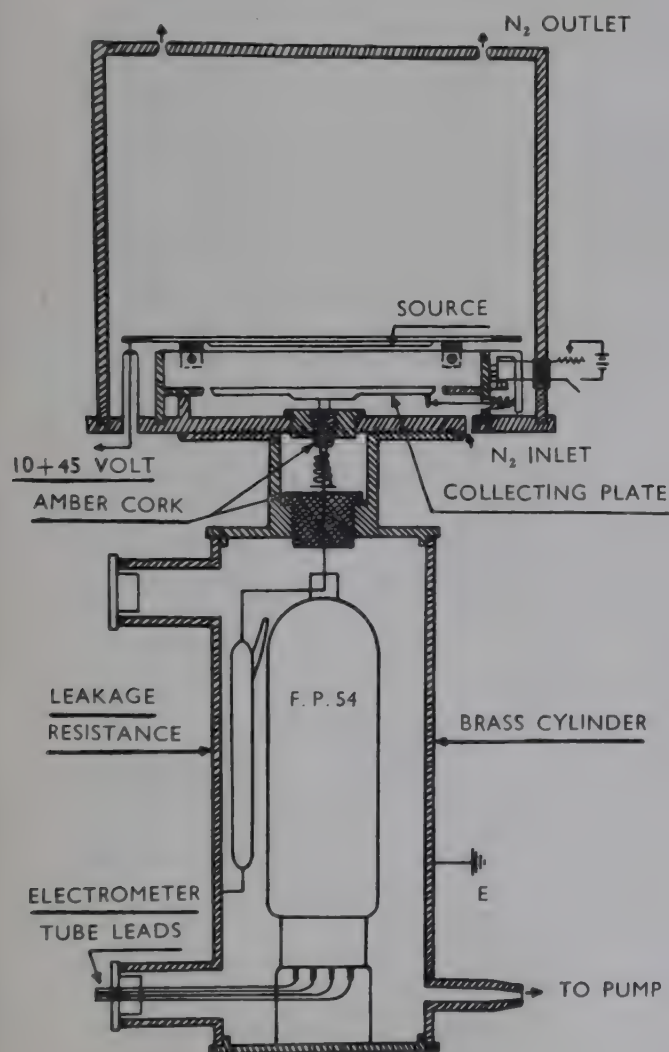


Fig. 5

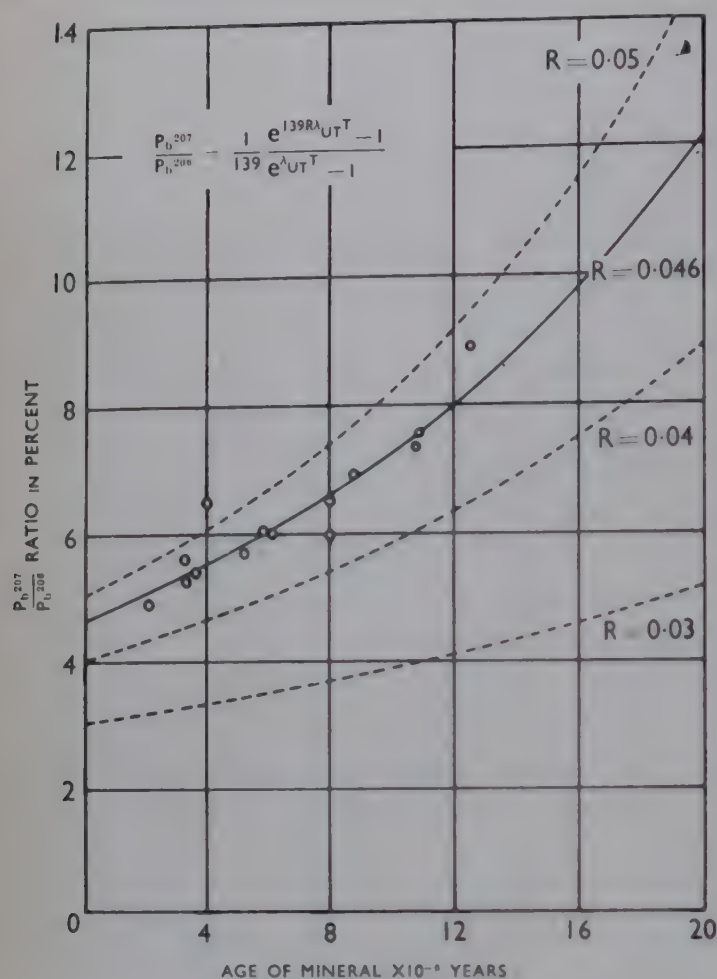


Fig. 6

is three and a half times faster, the accumulation of lead is not exactly in proportion but somewhat smaller. Nier has drawn a curve which we show in fig. 1 giving the actual calculated age taking the first and third factors into account against the ordinate of Pb^{207}/Pb^{206} ratio after correction for the presence of non-radiogenic lead. The age of this mineral is 90 million years from Nier's Curve in accordance with values by other methods.

Nier has developed a mass-spectrograph for routine studies of lead isotopes and has examined several minerals from all parts of the world for determining their ages by this method. The lead is usually used as a halide and the lead ions are obtained by electron bombardment. The mass ratios are measured in terms of ion currents, by an electrometer arrangement.

Measurement of Helium in Rocks.—Another method of measuring the amount of decay of uranium and thorium is to measure the amount of helium that has accumulated from the disintegration of uranium and thorium. For every uranium atom that disintegrates to lead, eight helium atomic nuclei are given out in the process. With thorium there are six helium atomic nuclei emitted for every atom of thorium. Helium accumulates six or eight

times faster than lead and can be estimated by methods of micro gas analysis. Helium estimations, however, suffer from a very serious defect. Helium is a very light gas and can pass through a lot of solid substances including glass and hence quite a large fraction of helium may have been lost from the mineral through the ages. Such loss of helium is very common and frequently give quite erroneous results when estimating geological ages. The helium method, however, leads to a minimum estimate which is sometimes useful, if care is taken to select minerals which are unweathered and show very little crystallisation. Paneth has pointed out certain minerals that contain natural helium which may give an over-estimate. Samarskite can be cited as an example of a mineral which, if obtained in unweathered condition, is likely to yield fairly consistent results if the mineral is not from a very old formation. The formula for young rocks is

$$T \text{ (in million years)} = \frac{8.8 \text{ He (in gms.)}}{\text{Uranium (in gms.)}} \text{ which yields}$$

for the Samarskite an age of 180 million years.

Keevil, Larsen, Evans and others have worked with extreme care on the helium ratio method and have made large number of measurements. They claim that with proper choice of minerals and due care, the error in age estimation may be reduced to about 10 to 15 per cent. Their results are sometimes extremely good. However, the objections to the helium method remains in some quarters as strong as before.

Let us see how far these different methods give us concordant results. Nier and Wells have examined a Samarskite from Connecticut, U.S.A. (Mineral 7 of fig. 6), analysed in the table by various methods as tabulated below.

Age in millions of years	Chemical				
	U + Th — Pb	U — Pb ²⁰⁸	Th — Pb ²⁰⁸	Pb ²⁰⁸ / Pb ²⁰⁷	U + Th — He
	350	253	266	280 ± 60	180

The results obtained by the helium method is given in the last column for comparison.

The example cited above is rather exceptional. Most minerals and their combination, the rocks, since their original formation from magma, undergo various changes (metamorphism) due to weathering action of water and air and due to their being brought under different conditions of pressure and temperature on account of folding and faulting of strata as well as due to the burying of the rocks under subsequent younger deposits. These changes may not only wear away the rocks or minerals, but change their composition and constitution as well. Certain uranium compounds are very soluble in water whereas the lead

produced from its disintegration is not so easily acted on by water. Such a rock may show greater proportion of lead content to the uranium and may be mistakenly attributed to a greater age. The lead 206/207 method will, to a certain extent, correct such errors. As we mentioned before helium escapes very easily from a rock and the helium estimate may be considerably lower than the actual value. Other types of changes can leach out the lead and cause underestimates or natural helium in rocks can give excessive estimations of age. Field evidences of the formation from which the rock or mineral is collected are thus of paramount importance in age determinations and the co-operation of geologists in interpreting the evidence is essential.

While we have mainly dealt with the major methods of measuring geologic time, it may be worthwhile to mention briefly some of the minor methods of interest and occasional usefulness. We have mentioned the first of these: the computation of heat loss due to the heat conductivity of the Earth's material. The modern and more precise variant of this method is that of geotherms and actual determination of heat generation and loss. This method is still in an embryonic stage and, though capable of giving valuable information, has not yet proved to be of much use in actual computations of age. The radio-activity of Potassium and Rubidium yields two independent methods. The accumulation of Strontium in Rubidium bearing mica has been studied and estimated by Hahn and Strassman in 1937. In one experiment 1 kgm. of old mica from Norway, belonging to early pre-Cambrian times, was examined. The mica contained 2 to 3% Rubidium, and 250 milligrams of Strontium Carbonate was extracted from the mineral. 99% of the Strontium was found to be the Strontium isotope 87 by mass-spectroscopic examination. If the Strontium isotope 87 is supposed to be formed by the beta radio-activity of Rubidium 87, then

$$\frac{\text{Number of Rubidium (87) atoms transformed to Sr (87)}}{\text{Number of Rubidium (87) atoms present}}$$

$$= \frac{\Delta N}{N} = \lambda t = \frac{.69t}{T}$$

calculating from above percentages of Rubidium and Strontium present in the mica one gets

$$\frac{\text{Sr (87)}}{\text{Rb (87)}} = \frac{1}{45} = \frac{.69t}{T}$$

The age of the mineral calculated on the basis of the half-value period of Rubidium as $\sim 10^{11}$ years exceeds that of 2×10^9 years the accepted age of the Earth. Hahn assumed that a certain amount of Rubidium had been lost causing the present discrepancy. It is interesting to note, however, that such methods in special cases may give an idea of age of the mineral. Geologists have studied the deposition of sediment and varves to estimate ages and duration of

epochs. Another method recently suggested by Ellsworth and amplified by Lane is the process of auto-oxidation of uranium from naturally occurring uranium dioxide to the trioxide. Each disintegrating uranium atom sets free two atoms of oxygen $\text{UO}_2 \rightarrow \text{Pb} + 8\text{He} + 2\text{O}$. These two atoms of oxygen can oxidise the neighbouring uranium dioxide in the mineral to the trioxide $2\text{UO}_2 + \text{O}_2 = 2\text{UO}_3$. Thus, according to Lane, one can estimate the number of uranium atoms that have disintegrated from the amount of trioxide of uranium present in the mineral. The age equation is T (in million years) $= 1.44 \times 10^4 \log \text{UO}/\text{Ut}$, where UO is the amount of U in dioxide form and Ut is the uranium in the trioxide form. The method has not yet been tried extensively nor has it been yet shown to give concordant results.

Another method which enjoyed a vogue about a decade or more ago is the observation of the intensity of discoloration of pleochroic haloes. These haloes are formed in mica due to very small inclusions of uranium or thorium. The ionisation of the emitted α -rays gradually discolours the mica and the amount of discoloration gives an estimate of age if the amount of intruding uranium or thorium can be estimated. As the inclusion may be normally as small as 10^{-19} gms. of uranium it is very difficult to get a reliable estimate of the quantity of radioactivity. This is the strongest criticism against this method.

All these minor methods may be of corroborative value but have not yet stood trial against extensive criticism that may be levelled against them. Mention may be made of the work recently started in this laboratory on these lines with measurements on radio-active contents of several minerals.

Further samples and information regarding them will be needed to work out comprehensive methods to deal with such problems. Co-operation of geologists and chemists to determine mode of occurrence, nature of alteration, geological epoch, etc., will be very necessary to such work. Further work on the determination of isotope ratios is also in contemplation.

It may be pointed out that such complicated analysis is not only desirable but extremely necessary to take various factors into account in estimating geological time. An extensive work of this type needs the co-operation of geologists, chemists and physicists working in a team to ensure taking into account various factors, like conditions of occurrence and associated minerals, chemical analysis, microanalysis, radio-active measurements and mass-spectrographic analysis of samples. Such a scheme of extensive work has been in operation for the last 12 years under the National Research Council of the U.S.A. in a Committee on the Measurement of Geologic Time under the Chairmanship of Prof. A. C. Lane with the collaboration of physicists like Nier and Evans, chemists like Baxter of Harvard and Sage and geologists like Keevil and Berman. Such an organisation with funds at its disposal would seem

to the author to be eminently desirable in this country for furthering such a work in an efficient and collaborative way. It is a matter of sincere congratulation that the Council of Scientific and Industrial Research of the Government of India has seen fit to make a grant for the development of the physical methods to the determination of the geological age. A great deal of work has to be done in this connection and co-ordination of efforts between the geologists and physicists has to be achieved. Some of the fundamental apparatus for routine determination, e.g. mass-spectrograph for isotope ratios, are still unavailable in this country.

It is hoped that with future co-operative efforts greater strides in the path of progress will be made in this field of fundamental work.

We wish to express our heartfelt thanks to Prof. D. N. Wadia for having gone through the paper, and helped us with very valuable suggestions in the preparation of the introductory parts.

REFERENCES

- BOWER (1939). Radio-activity of Potassium and Geologic Time. *Science*, **86**, 198.
 DALY. Igneous Rock.
 ELLSWORTH, H. (1925). Radioactive minerals as Geologic Indicators. *Amer. Journ., Sc.* **9**, 127.

- EVANS, R. D. (1935). Radio-activity of Solids. *Phys. Rev.*, **48**, 503.
 HARKER. Metamorphosis.
 HENDERSON, H. G. *et al* (1937). Studies of Pleochroic haloes. *Proc. Roy. Soc.*, **158**, 199.
 HOLMES. Physical Geology.
 HOLMES. The Age of the Earth.
 HOVELL, LANE *et al.* (1941). Symposia, Terrestrial Radio-activity. *Journ. Ap. Phy.*, **12**, 296.
 KEEVIL, N. B. (1939). The calculation of Geologic Age. *Amer. J. Sc.*, **237**, 195.
 — (1938). Economic Geology.
 LANE, A. C. (1941). The Earth shows its Age. *Science Progress*.
 LANE, A. C. AND URRY (1936). Estimation of Geologic Age. *Journ. Ch. Phy.*, **4**, 34.
 NAG *et al.* (1944). Radio-active Content of Indian Minerals. *Proc. Nat. Inst. Sc. Ind.*, **10**, 167.
 NATIONAL RESEARCH COUNCIL BULL. Common Geologic time annual reports, 1931-34.
 NIER, A. (1941). Isotopic Constitution of Pb and C. *Phys. Rev.*, **60**, 112.
 ROSE, M. *et al.* (1936). Isotopic const. of Pb from H.F.S. *Phys. Rev.*, **50**, 792.
 SAHNI, B. (1944). Tertiary Fossils in Salt Range. *Nature*, **153**, 462.
 SARKAR, P. B. (1941). On Age of some Radio-active Minerals. *Science and Culture*, **7**, 119.
 SHARMA, S. (1943). Classical List of Indian Minerals. *Tr. In. Ce. Soc.*, **3**, 90.
 URRY (1939). Ages by He-Method. *Bull. Geo. Soc. Am.*, **47**, 1217.
 WADIA, D. N. Geology of India.

82. ON THE PROPAGATION OF ELECTRO-MAGNETIC WAVES THROUGH THE UPPER ATMOSPHERE

M. N. SAHA*, B. K. BANERJEA AND U. C. GUHA

(*Ind. Jour. Phys.*, **21**, 181, 1947)

ABSTRACT

This paper reports a comprehensive working of the problems of an ionised atmosphere, traversed by a magnetic field, as in the case of the Earth's atmosphere. Expressions are deduced for electrical polarisation and complex conductivity for such an atmosphere when traversed by radio waves, in a tensor-form, as first suggested by Darwin. The equations of propagation of radio frequency waves through such a medium are obtained by the use of cardinal axes, and then the equations of vertical propagation are deduced. Expressions are obtained for refractive indices of ordinary and extraordinary waves, which agree with the expressions given by Appleton. Expressions are obtained for polarisation, absorption etc. of the radio waves travelling in the ionosphere. Curves are given for the polarisation ratio and refractive indices of the two waves as functions of the magnetic latitude of the place of observation.

INTRODUCTION

Ever since the classical works of Appleton (1932) and Hartree (1932), the problem of the propagation of e.m. waves in the ionosphere has received attention from numerous workers. Summaries of these works are available in various reports. Recently B. K. Banerjea (1947) made a critical and comparative study of the fundamental methods of Appleton (1932), Hartree (1932), Saha, Rai and Mathur (1937) and Saha and Banerjea (1945) and showed that these various methods can be deduced as special cases of

a general method developed according to Darwin's (1925) suggestion of treating the e.m. properties of the medium as tensor quantities. The present paper continues the treatment further and aims at giving a true wave formulation of the general problem. For the convenience of the reader some results of the previous works carried out by the senior author and his early collaborators are included so that no further references to these papers are needed. Part

*Fellow of the Indian Physical Society.

of the results mentioned in the earlier parts are not new, but have been derived in a novel, easier and unitary way.

The Displacement of the Ions in the Ionosphere

The equation of motion of the charged ions referred to any system of co-ordinates can be written as:

$$\frac{d^2 \rho}{dt^2} + \nu \frac{d\rho}{dt} + \frac{e}{mc} \left[\mathbf{H} \times \frac{d\rho}{dt} \right] = \frac{e}{m} \mathbf{E}, \quad \dots (1.1)$$

where ρ = displacement vector with components (ξ, η, ζ) .

e, m = magnitude of the charge and mass of the ion respectively.

ν = collision frequency of the ions.

$\mathbf{H}$ = Earth's magnetic field.

$\mathbf{E} = E_0 \cos pt$, electric vector of the incident electromagnetic wave.

The effect of the magnetic vector and the space charges have been omitted as usual. The notation conforms as closely as possible to those used by Appleton (1932) and Saha, Rai and Mathur (1937) and B. K. Banerjea (1947).

It can easily be verified that the solution of the above equation with $\mathbf{E} = E_0 \cos pt$ is the real part of the solution obtained with $\mathbf{E} = E_0 e^{ipt}$; we use $\mathbf{E}$ in this latter form because solution is then easy to obtain. The quantity analogous to the static conductivity now comes out as complex (Stratton, 1942), whose real part gives ordinary refractive index and the imaginary part gives deviation of the refractive index from unity.

Introducing the polarisation vector $\mathbf{P} = 4\pi N e \rho$ where N is the ion-concentration and using the abbreviations,

$$\frac{mp^2}{Ne^2} = \frac{4\pi p^2}{p_0^2} = \frac{4\pi}{r}, \quad p_0^2 = \frac{4\pi N e^2}{m}, \quad r = \frac{p_0^2}{p^2},$$

$$\nu/p = \delta, \quad \mathbf{I} - i\delta = \beta, \quad \dots (1.2)$$

$$\frac{e\mathbf{H}}{mc} = \mathbf{p}_h, \quad \frac{\mathbf{P}_h}{p} = \omega \text{ with components } \omega_x, \omega_y, \omega_z.$$

We get from equation (1.1) replacing ρ (ξ, η, ζ) by

$$\frac{1}{4\pi N e} (P_x, P_y, P_z)$$

$$\left. \begin{aligned} \beta P_x + i\omega_x P_y - i\omega_y P_z &= -E_x \\ -i\omega_x P_x + \beta P_y + i\omega_y P_z &= -E_y \\ i\omega_y P_x - i\omega_x P_y + \beta P_z &= -E_z \end{aligned} \right\} \dots (1.3)$$

The solution of these equations can be briefly written as

$$\mathbf{P} = \mathbf{A} \Delta \cdot \mathbf{E}, \quad \dots (1.4)$$

where $\mathbf{A} = \frac{r}{\beta(\beta^2 - \omega^2)}$ and Δ is a tensor given by the matrix,

$$\Delta = \begin{vmatrix} \omega_x^2 - \beta^2 & \omega_x \omega_y + i\beta \omega_z & \omega_x \omega_z - i\beta \omega_y \\ \omega_y \omega_x - i\beta \omega_z & \omega_y^2 - \beta^2 & \omega_y \omega_z + i\beta \omega_x \\ \omega_z \omega_x + i\beta \omega_y & \omega_z \omega_y - i\beta \omega_x & \omega_z^2 - \beta^2 \end{vmatrix} \quad (1.5)$$

It has been shown by Saha and Banerjea (1945) that the tensor possesses certain "Cardinal Axes" which may be denoted by 1, 2, 3. "1" is the direction of the earth's magnetic field, "2" is the line perpendicular to the magnetic meridian, and "3" is the line perpendicular to "1" lying in the magnetic meridian. The relation between these axes and the axes commonly used in ionospheric problems with XZ as magnetic meridian and OZ as vertical is shown in the diagram below:

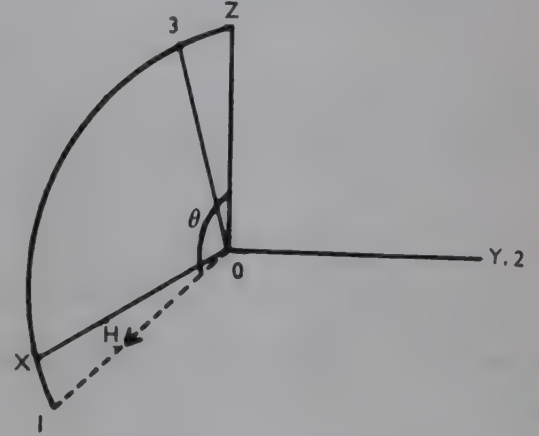


Fig. 1

Shows disposition of cardinal axes (1, 2, 3) with axes used generally in considering vertical propagation.

In this figure $\theta = \angle ZO1$ is called the angle of propagation. The axis O1 is always along the positive direction of $\mathbf{H}$. In general literature on ionospheric problems, the positive direction of $\mathbf{H}$ is generally not expressed quite clearly, with the result that the sense of rotation of the electric and magnetic vectors of the returning radio wave is left unclarified. In what follows the positive direction of $\mathbf{H}$ is along the positive direction of the magnetic lines of force, i.e. in the northern hemisphere it is downward and in the southern the reverse is the case.

Choice of these axes is equivalent to putting

$$w_1 = w, \quad w_2 = w_3 = 0,$$

where w_1, w_2, w_3 are the components of w along (1, 2, 3) axes. We have then

$$\Delta = - \begin{vmatrix} \beta^2 - \omega^2 & 0 & 0 \\ 0 & \beta^2 & i\beta \omega \\ 0 & -i\beta \omega & \beta^2 \end{vmatrix} \quad \dots (1.6)$$

The complex conductivity σ of the medium, defined by the equation

$$\sigma \cdot \mathbf{E} = \text{current} = -Ne \frac{d\rho}{dt} = -ipNe\rho = -\frac{ip}{4\pi} \mathbf{P} = -\frac{ip\mathbf{A}}{4\pi} \Delta \cdot \mathbf{E}$$

is a tensor quantity defined by the matrix,

$$\sigma = \frac{iNe^2}{m} \begin{vmatrix} \frac{1}{p-iv} & 0 & 0 \\ 0 & \frac{p-iv}{(p-iv)^2-p^2h} & \frac{-iph}{(p-iv)^2-p^2h} \\ 0 & \frac{iph}{(p-iv)^2-p^2h} & \frac{p-iv}{(p-iv)^2-p^2h} \end{vmatrix} \quad (1.7)$$

The steady current conductivity σ^* is obtained from above by putting $p=0$. We have

$$\sigma^* = -\frac{Ne^2}{m} \begin{vmatrix} \frac{1}{v} & 0 & 0 \\ 0 & \frac{v}{p_h^2+v^2} & \frac{p_n}{p_h^2+v^2} \\ 0 & \frac{-p_n}{p_h^2+v^2} & \frac{v}{p_h^2+v^2} \end{vmatrix} \quad \dots \quad (1.8)$$

Thus in the direction of the magnetic field, the steady current conductivity is $\frac{Ne^2}{mv}$. We have the components of current as

$$\begin{cases} i_1 = \frac{Ne^2}{mv} E_1 \\ i_2 = \frac{Ne^2}{m(p_h^2+v^2)} (\nu E_2 + p_n E_3) \\ i_3 = \frac{Ne^2}{m(p_h^2+v^2)} (-p_n E_2 + \nu E_3) \end{cases} \quad \dots \quad (1.9)$$

If $E_3=0$, we have $i_2 = \frac{Ne^2}{m(p_h^2+v^2)} \nu E_2$. The quantity $\frac{Ne^2 \nu}{m(p_h^2+v^2)}$ is known as transverse conductivity. We have besides, the current $i_3 = -\frac{Ne^2 p_n}{m(p_h^2+v^2)} E_2$ along the Z axis, though there may be no e.m.f. in that direction.

The Polarisation Vector—The polarisation vector P is defined as $P = \frac{4\pi i}{p} \sigma \cdot E$ and we can easily deduce that

$$E_1 = -\frac{\beta}{r} P_1, \quad E_2 \pm iE_3 = -\frac{\beta \mp \omega}{r} (P_2 \pm iP_3) \quad \dots \quad (1.10)$$

The Electric Displacement Vector and the Complex Dielectric Tensor—The electric displacement vector $D=E+P$ may be expressed as $D=K \cdot E$, where K is the complex dielectric tensor given by the matrix,

$$K = \begin{vmatrix} 1-r/\beta & 0 & 0 \\ 0 & 1-r\beta/(\beta^2-\omega^2) & ir\omega/(\beta^2-\omega^2) \\ 0 & -ir\omega/(\beta^2-\omega^2) & 1-r\beta/(\beta^2-\omega^2) \end{vmatrix} \quad \dots \quad (1.11)$$

2. THE MAXWELLIAN EQUATIONS

From the Maxwellian equations:

$$\nabla \times H = \frac{1}{c} \frac{\partial D}{\partial t}, \quad \nabla \times E = -\frac{1}{c} \frac{\partial H}{\partial t}, \quad \nabla \cdot D = \nabla \cdot H = 0 \quad \dots \quad (2.1)$$

We get by the usual methods, the equations of propagation for the electric and magnetic vectors in the form:

$$\begin{cases} \Delta^2 E_1 + \frac{\beta^2}{c^2} (1-r/\beta) E_1 = 0 \\ \nabla^2 (E_2 \pm iE_3) + \frac{\beta^2}{c^2} \left(1-r/(\beta \pm \omega)\right) (E_2 \pm iE_3) = 0 \\ \nabla^2 H + \frac{\beta^2}{c^2} H = -\frac{4\pi}{c} \nabla \times (\sigma \cdot E) \end{cases} \quad (2.2)$$

The Wave Equations for Vertical Propagation in any Latitude—Let us first confine ourselves to the propagation along the vertical Z-axis, so that ∇ and ∇^2 simply reduce to $\frac{d}{dz}$ and $\frac{d^2}{dz^2}$. Introducing the new variable $u=pz/c$, we get from (2.2)

$$\frac{d^2 E_1}{du^2} + \left(1 - \frac{r}{\beta}\right) E_1 = 0. \quad \dots \quad (2.3a)$$

$$\frac{d^2}{du^2} (E_2 + iE_3) + \left(1 - \frac{r}{\beta - \omega}\right) (E_2 + iE_3) = 0. \quad \dots \quad (2.3b)$$

$$\frac{d^2}{du^2} (E_2 - iE_3) + \left(1 - \frac{r}{\beta + \omega}\right) (E_2 - iE_3) = 0. \quad \dots \quad (2.3c)$$

The components of the vector E in two systems (1, 2, 3) and with XZ-plane as magnetic meridian and OZ as vertical are related as:

$$\begin{cases} E_1 = E_x \sin \theta + E_z \cos \theta; & E_x = E_1 \sin \theta - E_3 \cos \theta. \\ E_2 = E_y; & E_y = E_2. \\ E_3 = -E_x \cos \theta + E_z \sin \theta; & E_z = E_1 \cos \theta + E_3 \sin \theta. \\ \omega_x = \omega \sin \theta, & \omega_y = 0, & \omega_z = -\omega \cos \theta \end{cases} \quad (2.4)$$

The equations (2.3) as such are not suitable for use when we consider the propagation of plane waves, for such cases we have to use in conjunction with (2.2), the Maxwellian condition $\nabla \cdot D=0$. For vertical propagation, this reduces to $\frac{d}{dz} D_z=0$, i.e., $D_z=0$, since the steady components of D , if any, are unimportant in the study of the wave propagation:

From $D_z=0$ and (1.4) and (1.5) we have eliminating P_x, P_y, P_z and putting $w_y=0$.

$$E_z = \frac{rw_x}{c'} (-w_x E_x + i\beta E_y), \quad \dots \quad (2.5)$$

where $C'=\beta(\beta^2-w^2)-r(\beta^2-w_x^2)$.

Multiplying (2.3a) by $\sin \theta$ and the difference of (2.3b) and (2.3c) by $-\cos \theta$, adding the results and then replacing

E_1, E_2, E_3 by their equivalent expressions in terms of E_x, E_y, E_z from (2.4) we get after some simplification,

$$\frac{d^2 E_x}{du^2} + K_1 E_x - i L E_y = 0, \quad \dots (2.6)$$

$$\left. \begin{aligned} \text{where } K_1 &= 1 - r \frac{\beta^2 - r\beta - \omega^2 \sin^2 \theta}{C'} \\ L &= \frac{-r(\beta - r)\omega \cos \theta}{C'} \end{aligned} \right\} \quad \dots (2.7)$$

Again replacing E_2 and E_3 by E_x, E_y, E_z in equation (2.3b) from (2.4) and E_z by E_x and E_y from (2.2), we have after some work,

$$\frac{d^2 E_y}{du^2} + K_2 E_y + i L E_x = 0, \quad \dots (2.8)$$

$$\text{where } K_2 = 1 - r \frac{\beta^2 - r\beta}{C'}, \quad \dots (2.9)$$

Equation (2.6) and (2.8) were obtained explicitly in this form by Saha, Rai and Mathur (1937). Equivalent equations with vector components of the ordinary and extraordinary waves intermixed in each equation were obtained by Rydbeck (1944). But equations in this form do not help much in the understanding of the phenomena, unless the coupling term L between the variables vanishes. This takes place at $\theta = \pi/2$, *i.e.*, at the magnetic equator, where the equations of propagation become,

$$\left. \begin{aligned} \frac{d^2 E_x}{du^2} + \left(1 - \frac{r}{\beta}\right) E_x &= 0 \\ \frac{d^2 E_y}{du^2} + \left(1 - \frac{r}{\beta - \frac{\omega}{\beta - r}}\right) E_y &= 0 \end{aligned} \right\} \quad (2.10)$$

For the magnetic poles, $\theta = \pi$ and 0, and for these values of θ , $K_1 = K_2$; for $\theta = \pi$, *i.e.*, mag N-pole, the equation of propagation takes the form:

$$\frac{d^2}{du^2} (E_x \pm i E_y) + \left(1 - \frac{r}{\beta \mp \omega}\right) (E_x \pm i E_y) = 0. \quad \dots (2.11)$$

For $\theta = 0$, *i.e.*, mag. S-Pole, the equation similarly reduces to

$$\frac{d^2}{du^2} (E_x \pm i E_y) + \left(1 - \frac{r}{\beta \pm \omega}\right) (E_x \pm i E_y) = 0. \quad \dots (2.11a)$$

Equation in these forms were studied by Saha and Rai (1937), for the case when damping is negligible, *i.e.*, $\beta = 1$, from the wave mechanical point of view. The Chapman layer of ion-distribution was treated as a potential barrier and the penetration of the waves under certain simplifying assumptions were studied in the same way as Gamow did in his famous work on the "Penetration of the Potential Barrier of Nuclei of Atoms by High Energy particles."

Recently Rydbeck (1942) has studied these equations when the coupling term L vanishes; he has given an elaborate treatment of the wave equations for magnetic equator and taking a parabolic ion-layer and using Weber's parabolic functions he has obtained expressions for the reflection co-efficient, transmission co-efficient and phase retardation of the wave in a thin friction free parabolic layer. In the ray treatment of Appleton we practically confine ourselves to these two limiting cases, *viz.*, their quasi-longitudinal case is for $\theta = \pi, 0$, *i.e.*, $K_1 = K_2$ and their quasi-transverse case, *i.e.*, $\theta = \frac{\pi}{2}$, $L = 0$.

The following method will be found applicable to all stations. Multiplying both sides of (2.8) by " iF ," and adding to (2.6), where F is an indeterminate multiplier to be presently, determined, we have

$$\frac{d^2 E_x}{du^2} + iF \frac{d^2 E_y}{du^2} + (K_1 - FL) E_x + \left(K_2 - \frac{L}{F}\right) iF E_x = 0. \quad (2.12)$$

Now choose F in such a way that $K_1 - FL = K_2 - \frac{L}{F}$ so that F is given by the equation

$$F^2 - \frac{K_1 - K_2}{L} F - 1 = 0. \quad \dots (2.13)$$

$$\text{Put } \frac{K_1 - K_2}{L} = \frac{\omega \sin^2 \theta}{(r - \beta) \cos \theta} = 2G = 2g \cos \alpha \sin \alpha,$$

$$\text{where } g = \frac{\omega \sin^2 \theta}{(r - 1) \cos}, \quad \tan \alpha = \frac{\delta}{1 - r}. \quad \dots (2.14)$$

Let F_1, F_2 be the roots of equation (2.13). Then

$$\begin{aligned} F_1, F_2 &= G \pm \sqrt{1 + G^2} \\ &= g \pm \sqrt{1 + g^2} \quad \text{for } \delta = 0. \quad \dots (2.15) \end{aligned}$$

Now turning to equation (2.12) we can rewrite it in the form

$$\frac{d^2}{du^2} (E_x + iF E_y) + q^2 (E_x + iF E_y) - 2i \frac{dF}{du} \frac{dE_y}{du} - i \frac{d^2 F}{du^2} E_y = 0 \quad \dots (2.16)$$

where q has the two values given by

$$\begin{aligned} q_1^2 &= K_2 - \frac{L}{F_1} = K_2 + LF_2 = 1 - \frac{r}{c'} (\beta - \gamma) (\beta + \omega \cos \theta F_2) \\ &= 1 - \frac{r}{\beta + \omega \cos \theta F_1}. \quad \dots (2.17) \end{aligned}$$

$$\begin{aligned} q_2^2 &= K_1 - \frac{L}{F_2} = K_1 + LF_1 = 1 - \frac{r}{c'} (\beta - r) (\beta + \omega \cos \theta F_1) \\ &= 1 - \frac{r}{\beta + \omega \cos \theta F_2}, \quad \dots (2.18) \end{aligned}$$

for $C' = (\beta - r) (\beta + \omega \cos \theta F_1) (\beta + \omega \cos \theta F_2)$.

In those cases where the quantities $\frac{dF}{du}$, $\frac{d^2F}{du^2}$ can be neglected, the equations can be written as

$$\left. \begin{aligned} \frac{d^2}{du^2} (E_x + iF_1 E_y) + q_1^2 (E_x + iF_1 E_y) &= 0 \\ \frac{d^2}{du^2} (E_x + iF_2 E_y) + q_2^2 (E_x + iF_2 E_y) &= 0 \end{aligned} \right\} \dots (2.16a)$$

These signify that the beam is broken up into two, with the refractive indices q_1 , and q_2 , and polarisations determined by F_1 and F_2 (*Vide* § 4).

We next proceed to discuss the case of friction free atmosphere. In this case we have

$$q_1^2 = 1 - \frac{r}{1 + \omega \cos \theta F_1} \dots (2.17a)$$

$$q_2^2 = 1 - \frac{r}{1 + \omega \cos \theta F_2} \dots (2.18a)$$

Both q_1 , q_2 are to be continuous functions of r . We find from the expression for g , that for $r \rightarrow 1$, $g \rightarrow \infty$. At this point, q_1^2 , q_2^2 should obey the condition of continuity, i.e.,

$$\lim_{r \rightarrow 1-0} (q_1^2, q_2^2) = \lim_{r \rightarrow 1+0} (q_1^2, q_2^2).$$

Taking first q_1 , we find that if we take for the region $r=0$ to $r=1$

$$F_1 = g - \sqrt{1+g^2}, \text{ consequently } q_1^2 = 1 - \frac{r}{1 - \omega \cos \theta (\sqrt{1+g^2} - g)} \dots (2.17b)$$

Then q_1 varies from 1 to 0 in the domain $r=0$ to 1. As the value is to be continuous, and since g on crossing over to $r=1+0$, becomes negative, we find that for this region ($r>0$) we should put

$$F_1 = \sqrt{1+g^2} - |g|$$

$$\text{i.e., } q_1^2 = 1 - \frac{r}{1 + \omega \cos \theta (\sqrt{1+g^2} - |g|)} \dots (2.17c)$$

These expressions for q_1^2 has no singularity at any point and it is identical with the expression for the refractive index of the ordinary wave as given by Appleton. A $(r-q_1^2)$ curve for different values of θ from expressions (2.17 b, c) is given in Fig. 2, for $\omega < 1$, and $\omega > 1$.

For the other beam we can now substitute the corresponding value of F_2 , we obtain:

$$q_2^2 = 1 - \frac{r}{1 + \omega \cos \theta F_2} = 1 - \frac{r}{1 + \omega \cos \theta (\sqrt{1+g^2} + g)}$$

for $r \geq 1$.. (2.18b)

$$= 1 - \frac{r}{1 - \omega \cos \theta (\sqrt{1+g^2} + |g|)} \text{ for } r > 1. \dots (2.18c)$$

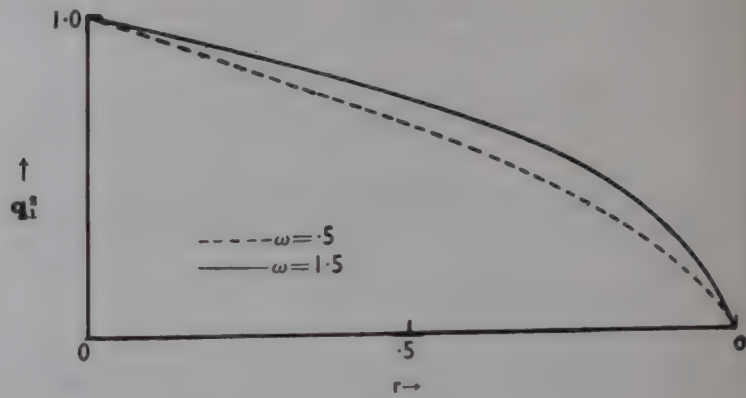


Fig. 2

Variation of the square of the refractive index for the o-wave with electron concentration $r = \left(\frac{4\pi e^2}{m\beta^2} N \right)$, for $p_h/p = \omega < 1$ (here .5) and $\omega > 1$ (here 1.5)

It can be easily shown that for $\omega < 1$, $(r-q_2^2)$ —curve starts from $(0, 1)$ passes through $(1-\omega, 0)$ and a point of infinite singularity at $r = \frac{1 - \omega^2 \cos^2 \theta}{1 - \omega^2}$ where it passes from $-\infty$ to $+\infty$, passes through the point $(1, 1)$ and $(1+\omega, 0)$ for all values of θ .

q_2^2 has therefore to be identified with the square of the refractive index of the extraordinary wave (Fig. 3).

For $\omega > 1$, we find that the curve passes through $(0, 1)$ and $(1, 1)$, between $r=0$, and 1, $q_2^2 > 1$ but after $(1, 1)$ the value of q_2^2 becomes less than unity and gradually tends to the value zero at $r=1+\omega$, after which it is negative (Fig. 3).

The quantities $g(\omega, r, \theta)$, $-F = \sqrt{1+g^2} - |g|$ which occur in this work are functions of ω , r and θ .

In Table 1, the function $g(\omega, 0, \theta)$ has been given for various values of ω and θ . To obtain $g(\omega, r, \theta)$ we have to divide $g(\omega, 0, \theta)$ by $(r-1)$.

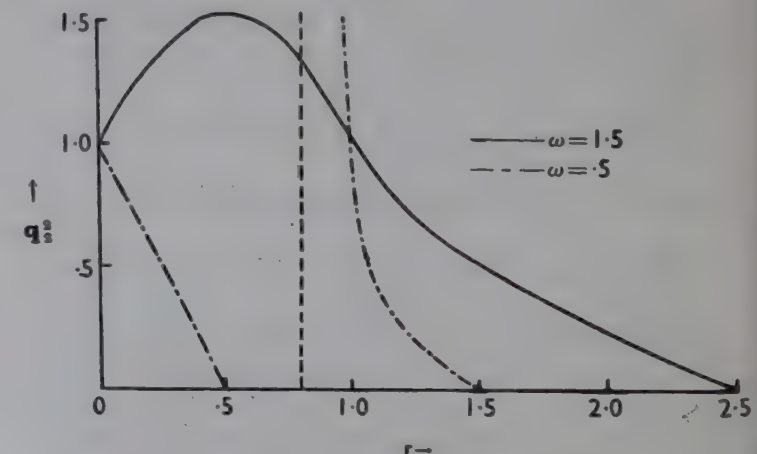


Fig. 3

Variation of the square of the refractive index for the e-wave with electron concentration $r = \left(\frac{4\pi e^2}{m\beta^2} N \right)$ for $p_h/p = \omega < 1$ (here .5) and $p_h/p = \omega > 1$ (here 1.5).

TABLE I

$$g = \omega \cos^2 \theta / 2 \sin \theta, \quad r = 0$$

θ°	$\omega = .1$	$\omega = .2$	$\omega = .3$	$\omega = .5$	$\omega = .8$	$\omega = 1.0$	$\omega = 1.5$	$\omega = 2$	$\omega = 5$	$\omega = 10$	$\omega = 20$	$\omega = 50$	$\omega = 100$
91°	2.8640	5.7270	8.591	14.315	22.908	28.635	42.955	57.270	143.15	286.35	572.70	1431.5	2863.5
92°	1.4310	2.8620	4.293	7.155	11.448	14.310	21.465	28.620	71.55	143.10	286.20	715.5	1431.0
93°	.9525	1.9050	2.858	4.763	7.620	9.525	14.290	19.050	47.63	95.25	190.50	476.3	952.5
94°	.7135	1.4270	2.141	3.568	5.708	7.135	10.705	14.270	35.68	71.35	142.70	356.3	713.5
95°	.5695	1.1390	1.709	2.848	4.556	5.695	8.545	11.390	28.48	56.95	113.90	284.8	569.5
190°	.2793	.5586	.838	1.397	2.234	2.793	4.190	5.586	13.97	27.93	55.86	139.7	279.3
105°	.1802	.3604	.541	.901	1.442	1.802	2.795	3.604	9.01	18.02	36.04	90.1	180.2
110°	.1291	.2581	.387	.645	1.032	1.291	1.935	2.581	6.45	12.91	25.81	64.5	129.1
115°	.0972	.1944	.292	.486	.777	.972	1.460	1.944	4.86	0.72	19.44	48.6	97.2
120°	.0750	.1500	.225	.375	.600	.750	1.113	1.500	3.75	7.50	15.00	37.5	75.0
125°	.0585	.1170	.176	.293	.468	.585	.880	1.170	2.93	5.85	11.70	29.3	58.5
130°	.0457	.0913	.137	.228	.365	.457	.685	.913	2.28	4.57	9.13	22.8	45.7
135°	.0354	.0707	.106	.177	.283	.354	.530	.707	1.77	3.54	7.07	17.7	35.4
140°	.0270	.0539	.081	.135	.216	.270	.405	.539	1.35	2.70	5.39	13.5	27.0
145°	.0201	.0402	.060	.100	.161	.201	.300	.402	1.00	2.01	4.02	10.0	20.1
150°	.0144	.0289	.043	.072	.115	.144	.215	.289	.72	1.44	2.89	7.20	14.4
155°	.0099	.0197	.030	.049	.079	.099	.150	.197	.49	.99	1.97	4.90	9.9
160°	.0062	.0125	.019	.031	.050	.062	.095	.125	.31	.62	1.25	3.11	6.2
165°	.0035	.0069	.010	.017	.028	.035	.050	.069	.17	.35	.69	1.72	3.5
170°	.0015	.0031	.005	.008	.012	.015	.025	.031	.03	.15	.31	.80	1.5
175°	.0004	.0008	.001	.002	.003	.004	.005	.008	.02	.04	.08	.21	.4
176°	.0002	.0004	.001	.001	.002	.002	.004	.004	.01	.02	.04	.10	.2
177°	.0001	.0003	.000	.001	.001	.001	.002	.003	.99(5)	.01	.02	.05	.1
178°	.0001	.0001	.000	.000	.000	.001	.001	.001	.00(3)	.00(6)	.01	.03	.0(6)
179°	.0000	.0000	.000	.000	.000	.000	.000	.000	.00	.00	.00	.00	.00
180°	.0000	.0000	.000	.000	.000	.000	.000	.000	.00	.00	.00	.00	.00

3. FINITE DAMPING

We next discuss the case when $\delta \leq 0$, and in so doing we have to formulate the expressions for polarisation ratios and refractive indices in such a way that if $\delta \rightarrow 0$, these general expressions should reduce to those discussed in the previous section.

In this case F_1 and F_2 are complex roots of the equation (2.13). Let us put

$$F_1 = -\rho e^{i\phi}, \text{ and consequently } F_2 = \frac{1}{\rho} e^{-i\phi}, \quad \dots (3.1)$$

since $F_1 F_2 = -1$, with the condition that ρ is always positive. In the particular case $\delta = 0$, we have $\phi = 0$ or π . Since F_1 is negative for $r < 1$, therefore $\phi = 0$ for $r < 1$. Again F_1 is positive for $r > 1$, therefore, $\phi = \pi$ for $r > 1$. So we get for $\delta = 0$,

$$\rho = \sqrt{1 + g^2} - |g| \text{ for } r > 1, \text{ and } < 1.$$

Now

$$F_1 + F_2 = \frac{1}{\rho} e^{i\phi} - \rho e^{-i\phi} = 2g \cos \alpha e^{i\alpha} = 2G.$$

Equating real and imaginary parts,

$$(1-r) \cos \phi \left(\frac{1}{\rho} - \rho \right) - \delta \sin \phi \left(\frac{1}{\rho} + \rho \right) = -\frac{\omega \sin^2 \theta}{\cos \theta} \quad (3.2)$$

$$\delta \cos \phi \left(\frac{1}{\rho} - \rho \right) + (1-r) \sin \phi \left(\frac{1}{\rho} + \rho \right) = 0,$$

$$\text{or } \cos \phi \{ (1/\rho) - \rho \} = 2g \cos^2 \alpha,$$

$$\sin \phi \{ (1/\rho) + \rho \} = -2g \sin \alpha \cos \alpha.$$

Solving the above equations (3.2) we get

$$\left. \begin{aligned} \sin^2 \phi &= \frac{2g^2 \sin^2 \alpha}{1 + g^2 + \sqrt{1 + 2g^2 \cos 2\alpha + g^4}} \\ \tan \phi &= -\frac{1 - \rho^2}{1 + \rho^2} \tan \alpha \end{aligned} \right\} \dots (3.3)$$

$$\text{and } \rho = \pm \sqrt{1 + g^2 \cos^2 \alpha - \sin^2 \phi} \pm \sqrt{g^2 \cos^2 \alpha - \sin^2 \phi}. \quad (3.4)$$

This expression for ρ can reduce to the corresponding relation for $\delta = 0$ only if we take

$$\rho = \sqrt{1 + g^2 \cos^2 \alpha - \sin^2 \phi} - \sqrt{g^2 \cos^2 \alpha - \sin^2 \phi}. \quad (3.4a)$$

Hence $1/\rho - \rho = 2\sqrt{g^2 \cos^2 \alpha - \sin^2 \phi} > 0$, for all values of α and g . Thus $\rho < 1$. Then returning to the equations (3.2), we have for northern hemisphere for the region $r \geq 1$, i.e., $g > 0$

$$\cos \phi \geq 0, \sin \phi < 0, \text{ i.e., } 3\pi/2 < \phi < 2\pi,$$

and for the region $r \leq 1$, i.e., $g < 0$

$$\cos \phi \geq 0, \sin \phi < 0, \text{ i.e., } \pi \leq \phi < 3\pi/2.$$

The case in the southern hemisphere is just the opposite. The results can be tabulated as shown in Table II.

With these complex expressions for F_1 and F_2 which reduce to the expressions discussed in the previous chapter, we get the ordinary and extraordinary complex refractive indices as

$$q_0^2 = 1 - \frac{r}{\beta + \omega \cos \theta F_1} = 1 - \frac{r}{\beta - \omega \rho \cos \theta e^{i\phi}} = 1 - \frac{r}{X_0 - iY_0} \quad (3.5)$$

TABLE II

θ	r	$g = \frac{\omega \sin^2 \theta}{2(r-1) \cos \theta}$	$\delta = 0$		$\delta > 0$	
			$\rho = -F_1$	ϕ	ρ	ϕ
N. H.	< 1	(+)	$\sqrt{1+g^2}-g$	0		$3/2\pi < \phi \leq 2\pi$
$\pi/2 \leq \theta \leq \pi$	> 1	(-)	$\sqrt{1+g^2}+ g $	π	$\sqrt{1+g^2 \cos^2 \alpha - \sin^2 \phi}$	$\pi \leq \phi \leq 3/2\pi$
S. H.	< 1	(-)	$\sqrt{1+g^2}+ g $	π	$-\sqrt{g^2 \cos^2 \alpha - \sin^2 \phi}$	$0 < \phi < \pi/2$
$0 \leq \theta \leq \pi/2$	> 1	(+)	$\sqrt{1+g^2}-g$	0		$\pi/2 < \phi < \pi$

where $X_0 = 1 - \omega \rho \cos \theta \cos \phi$, $Y_0 = \delta + \omega \rho \cos \theta \sin \phi$.

$$q_0^2 = 1 - \frac{r}{\beta + \omega \cos \theta F_2} = 1 - \frac{r}{\beta + \omega/\rho \cos \theta e^{-i\phi}} = 1 - \frac{r}{X_0 - iY_0} \quad \dots (3.6)$$

where $X_0 = 1 + \omega/\rho \cos \theta \cos \phi$, $Y_0 = \delta + \omega/\rho \cos \theta \sin \phi$.

Following Booker, we may put $q = \mu - (ick/\rho)$.

$$\text{Then } \mu^2 - \frac{c^2 k^2}{\rho^2} = 1 - \frac{rX}{X^2 + Y^2}, \quad \frac{2\mu ck}{\rho} = \frac{rX}{X^2 + Y^2} \quad \dots (3.7)$$

and for the non-deviating region, where $ck/\rho < 1$

$$k = \frac{\rho}{2c} \left(\frac{1}{\mu} - \mu \right) \frac{Y}{X}, \quad \mu^2 = 1 - \frac{rX}{X^2 + Y^2}.$$

We have thus for the non-deviating region:

$$\left. \begin{aligned} \mu_0^2 &= 1 - r \frac{1 - \omega \rho \cos \theta \cos \phi}{(1 - \omega \rho \cos \theta \cos \phi)^2 + (\delta + \rho \omega \cos \theta \sin \phi)^2} \\ k_0 &= \frac{\rho}{2c} \left(\frac{1}{\mu} - \mu \right) \frac{\delta + \rho \omega \cos \theta \sin \phi}{1 - \omega \rho \cos \theta \cos \phi} \end{aligned} \right\} \quad (3.8)$$

$$\left. \begin{aligned} \mu_e^2 &= 1 - r \frac{1 + \omega/\rho \cos \theta \cos \phi}{(1 + \omega/\rho \cos \theta \cos \phi)^2 + (\delta + \omega/\rho \cos \theta \sin \phi)^2} \\ k_e &= \frac{\rho}{2c} \left(\frac{1}{\mu_e} - \mu_e \right) \frac{\delta + \omega/\rho \cos \theta \sin \phi}{(1 + \omega/\rho \cos \theta \cos \phi)} \end{aligned} \right\} \quad (3.9)$$

The correctness of the above expressions can be tested for special cases:

For the magnetic equator, $\theta = \pi/2$ we have from (3.4a), $\rho = 0$ and $\frac{\sin \theta}{\rho} e^{-i\phi} = \frac{\omega}{\beta - r}$. Hence, we get the equations (2.10), as special cases of (2.16a). For the magnetic north pole, $\theta = \pi$, $\rho = 1$, $\phi = \pi$, hence (2.16a) reduce to equations (2.11). For the magnetic south pole $\theta = 0$, $\rho = 1$, $\phi = 0$, hence (2.16a) reduce to equations (2.11a).

4. POLARISATION

Let us next discuss the polarisation of the down-coming wave for any station for a stratified, slowly varying ionosphere with finite damping. Since the e.m. waves which are propagated in such a medium are not transverse in the electric vector E , but are transverse in the magnetic vector H and in the method of detection, the H vector is utilized, it is customary to express the polarisation of the waves with respect to the latter. So we start with the equations of propagation of the magnetic vector, viz.,

$$\frac{d^2 H_x}{du^2} + K_2 H_x - iLH_y = 0 \quad \dots (4.1)$$

$$\frac{d^2 H_y}{du^2} + K_1 H_y + iLH_x = 0 \quad \dots (4.2)$$

in place of the corresponding equations (2.6) and (2.8) for the electric vector. Equations (4.1) and (4.2) follow immediately from (2.6) and (2.8) and (2.1). Eliminating H_y and H_x from (4.2) and (4.3) respectively we get

$$\frac{d^4 H_x}{du^4} + (K_1 + K_2) \frac{d^2 H_x}{du^2} + (K_1 K_2 - L^2) H_x = 0 \quad \dots (4.3)$$

$$\text{and } \frac{d^4 H_y}{du^4} + (K_1 + K_2) \frac{d^2 H_y}{du^2} + (K_1 K_2 - L^2) H_y = 0 \quad \dots (4.4)$$

where the derivatives of K_1 , K_2 and L have been neglected as before. The general solutions of (4.3) and (4.4) are

$$H_x = A_1 e^{is_1 u} + A_2 e^{+is_2 u} + A_3 e^{-is_1 u} + A_4 e^{-is_2 u}$$

$$H_y = B_1 e^{is_1 u} + B_2 e^{+is_2 u} + B_3 e^{-is_1 u} + B_4 e^{-is_2 u}$$

where

$$s_1^2 = \frac{K_1 + K_2 - \sqrt{(K_1 - K_2)^2 + 4L^2}}{2}$$

$$s_2^2 = \frac{K_1 + K_2 + \sqrt{(K_1 - K_2)^2 + 4L^2}}{2}$$

It can be easily shown that

$$s_1^2 = q_1^2, \quad s_2^2 = q_2^2.$$

Retaining only the solutions for the downcoming waves, we get

$$H_x = A_1 e^{iq_2 u} + A_2 e^{iq_1 u} \quad \dots (4.5)$$

$$H_y = B_1 e^{iq_2 u} + B_2 e^{iq_1 u} \quad \dots (4.6)$$

where q_1 and q_2 are those roots of s_1^2 and s_2^2 respectively which have the imaginary parts positive. Substituting (4.5) and (4.6) in (4.1) we get,

$$(-q_1^2 A_2 + K_2 A_2 - iLB_2) e^{iq_1 u} + (-q_2^2 A_1 + K_2 A_1 - iLB_1) e^{iq_2 u} = 0,$$

which being an identity in u yields

$$-q_1^2 A_2 + K_2 A_2 - iLB_2 = 0$$

$$-q_2^2 A_1 + K_2 A_1 - iLB_1 = 0$$

whence we have, referring back to (4.1) and (4.2),

$$\frac{B_1}{A_1} = i \frac{q_2^2 - K_2}{L}; \quad \frac{B_2}{A_2} = i \frac{q_1^2 - K_2}{L} \quad \dots (4.7)$$

From the general solutions of (4.1) and (4.2) it is evident that these equations represent two waves given by

$$H_x^{(1)} = A_1 e^{iq_2 u}, \quad H_y^{(1)} = B_1 e^{iq_1 u}$$

$$H_x^{(2)} = A_2 e^{iq_1 u}, \quad H_y^{(2)} = B_2 e^{iq_2 u}$$

travelling with complex phase velocities c/q_2 and c/q_1 respectively. Following the nomenclature adopted before $H_x^{(1)}$ & $H_y^{(1)}$ combine to give the downcoming extraordinary wave and $H_x^{(2)}$ & $H_y^{(2)}$ give the downcoming ordinary wave, and the polarisation ratios for the two waves are

$$\frac{H_y^{(0)}}{H_x^{(0)}} = \frac{B_2}{A_2} = i \frac{q_1^2 - K_2}{L} = iF_1$$

$$\frac{H_y^e}{H_x^e} = \frac{B_1}{A_1} = i \frac{q_2^2 - K_2}{L} = iF_2.$$

Taking $H_x^{(0)} = R_{ox} e^{i(\gamma_{ox} + pt)}$, $H_y^{(0)} = R_{oy} e^{i(\gamma_{oy} + pt)}$ where R_{ox} , R_{oy} , γ_{ox} and γ_{oy} are real functions of u , we get

$$H_x^{(0)} = R_{ox} \cos(\gamma_{ox} + pt), \quad H_y^{(0)} = R_{oy} \cos(\gamma_{oy} + pt)$$

as the two true solutions of the problem with

$$E = E_0 \cos pt \text{ in place of } E = E_0 e^{ipt}.$$

$$\text{Hence } \frac{H_y^{(0)}}{H_x^{(0)}} = \frac{R_{oy}}{R_{ox}} e^{i(\gamma_{oy} - \gamma_{ox})} = iF_1 = -i\rho e^{i\phi} = \rho e^{i(\phi - \pi/2)},$$

$$\text{whence } \rho = \frac{R_{oy}}{R_{ox}}$$

$$\text{and } \gamma_{oy} - \gamma_{ox} = \phi - \frac{\pi}{2}$$

are the ratio of the axes and the constant phase difference between the y and x components of the magnetic vector

respectively. The equation of the polarisation ellipse for the ordinary wave follows immediately by eliminating " pt " between the two equations in (4.8): We have

$$H_x^{(0)2} - \frac{2H_x^{(0)}H_y^{(0)}}{\rho} \sin \phi + \frac{H_y^{(0)2}}{\rho} = R_{ox}^2 \cos^2 \phi. \quad \dots (4.9)$$

This equation shows that the axes of the ellipse are tilted to the respective y and x axes, the amount ψ_0 of tilt to the y axis being given by

$$\tan 2\psi_0 = -\frac{2\rho \sin \phi}{1 - \rho^2}. \quad (4.10)$$

The points of contact of this ellipse with the circumscribed rectangle are (Fig. 4) respectively $(\pm R_{ox} \sin \phi, \pm R_{ox} \rho)$ and $(\pm R_{ox} \pm \rho R_{ox} \sin \phi)$

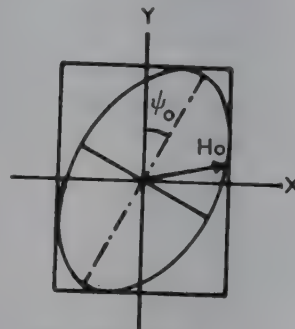


Fig. 4

Polarisation ellipse for the reflected o-wave (northern hemisphere)

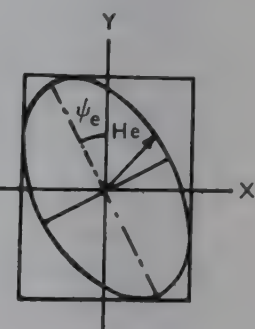


Fig. 5

Polarisation ellipse for the reflected o-wave (southern hemisphere)

For the other wave

$$\rho_e = \frac{R_{ey}}{R_{ex}}, \quad \gamma_{ey} - \gamma_{ex} = \phi + \frac{\pi}{2}$$

and it can easily be shown that

$$\rho_e = \frac{1}{\rho} \text{ and } (\gamma_{ey} - \gamma_{ex}) - (\gamma_{oy} - \gamma_{ox}) = \pi \quad (4.11)$$

consequently the equation of the polarisation ellipse for the e-wave is

$$\frac{H_x^2}{\rho^2} + \frac{2H_x^e H_y^e}{\rho} \sin \phi + H_y^2 = \frac{R_{ex}^2}{\rho^2} \cos^2 \phi$$

which shows the same ellipse rotated through an angle $\pi/2$. For this ellipse (Fig. 5) the angle of tilt and the points of contact with the circumscribed rectangle are given by:

$$\tan 2\psi_e = -\frac{2\rho \sin \phi}{1 - \rho^2} = \tan(2\psi_0 + \pi) \quad (4.13)$$

$$\text{and } \left(\pm R_e \sin \phi, \pm \frac{R_e}{\rho} \right), \left(\pm R_{ox}, \pm \frac{R_e}{\rho} \sin \phi \right)$$

In the experimental methods of determining the ratio of the axes of the polarisation ellipse, it is generally assumed

that the polarisation of the downcoming wave is mainly determined by the lowest layers of the ionosphere where N the ion concentration tends to vanish. Recently Eckersley (1945) has determined the polarisation of the downcoming waves for $p=6.1, 6.4$ and 7.6 Mc. and has remarked that in order to agree with his experimental results, the polarisation of the downcoming wave should be determined not by the lowest layer of the ionised strata but somewhere inside. Since there is as yet no definite and convincing evidence either experimental or theoretical, of the particular strata or the entire layer fixing the polarisation, we have plotted ρ , the ratio of the axes for the o-wave as a function of $\theta' = \theta - \frac{\pi}{2}$, the magnetic latitude of the place of observations for various values of ω , for τ , i.e., $N \rightarrow 0$.

Sense of rotation of the polarisation ellipse can be inferred from equations (4.8). Since the damping has no effect on the sense of rotation of the magnetic vector, we infer the sense of rotation for the case where damping is absent. In this case for northern hemisphere $\phi=0$, and hence equation (4.8) gives

$$H_x^o = R_{ox} \cos (\gamma_{ox} + pt)$$

$$H_y^{(o)} = \rho R_{ox} \sin (\gamma_{ox} + pt).$$

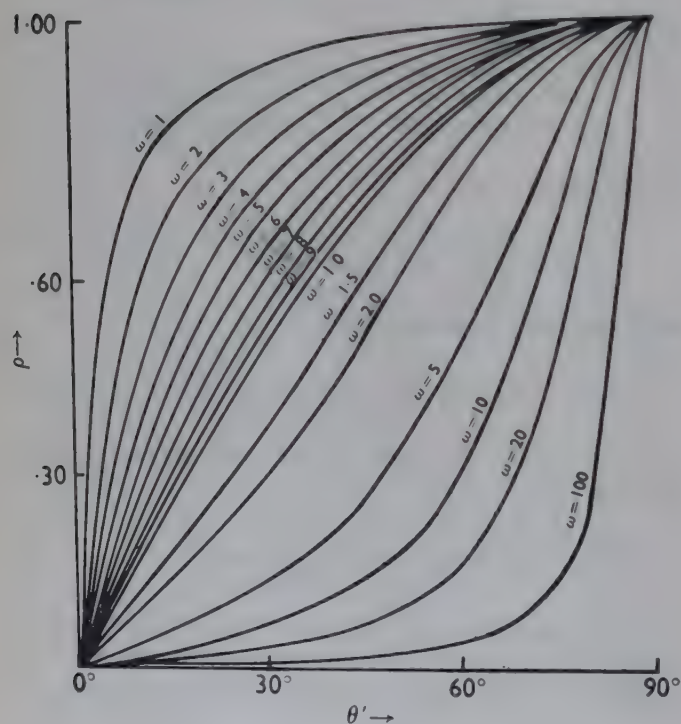


Fig. 6

Variation of the polarisation ratio $= \rho \sqrt{1+g^2} - |g|$ where $g = \frac{\omega \sin^2 \theta}{2 \cos \theta}$ for various values of $\omega = p_h/p$ for different angles of propagation. $\rho \rightarrow 1$ means circular polarisation.

Hence as t increases from 0, H_x^o decreases from $R_{ox} \cos \gamma_{ox}$ to 0 and remains positive, while $H_y^{(o)}$ increases from $\rho R_{ox} \sin \gamma_{ox}$ to ρR_{ox} showing that the vector H_x^o , whose components are H_x^o and H_y^o and which describes the ellipse given by (4.9) is moving in the anticlockwise direction. Thus for all waves received in the northern hemisphere the downcoming ordinary wave is polarised in the anticlockwise direction as viewed along the direction of propagation. For the extraordinary wave,

$$H_x^e = R_{ex} \cos (\gamma_{ex} + pt)$$

$$H_y^e = -\frac{R_{ex}}{\rho} \sin (\gamma_{ex} + pt).$$

Hence as t increases from 0, H_x^e decreases as before but H_y^e becomes more and more negative showing that the vector H^e whose components are H_x^e and H_y^e and which describes the ellipse given by (4.12) moves in the clockwise direction. Thus for all stations in the northern hemisphere, the downcoming e-wave is polarised right handed as viewed along the direction of propagation.

For the southern hemisphere the sense of the rotation of the two ellipses will be just opposite since $\phi=\pi$ for $\delta=0$ in the southern hemisphere in place of $\phi=0$ for $\delta=0$ in the northern hemisphere.

ACKNOWLEDGEMENT

Two of us, B. K. Banerjea and U. C. Guha, have been the recipients of two Research scholarships from the Radio Research Committee of the Council of Scientific and Industrial Research (India) and wish to express their thanks to the Council for facility to work and permission to publish this paper.

Palit Laboratory of Physics,
Calcutta University.

REFERENCES

- APPLETON 1932, *Jour. Inst. Elec. Eng.*, **71**, 646.
- BANERJEA 1947, *Proc. Roy. Soc. A.*, **196**, 67.
- BOOKER 1936, *Proc. Roy. Soc. A.*, **155**, 235.
- ECKERSLEY 1945, *Proc. Roy. Soc. A.*, **184**, 196.
- DARWIN 1925, *Trans. Camb. Phil. Soc.*, **23**, 137.
- HARTREE 1932, *Proc. Camb. Phil. Soc.*, **29**, 143.
- RYDBECK 1940, *J. Applied Physics*, **13**, 577.
- SAHA, RAI AND MATHUR 1937, *Nat. Inst. Sci. (India)*, **4**, 53.
- SAHA AND RAI 1937, *Nat. Inst. Sci. (India)*, **4**, 319.
- SAHA AND BANERJEA 1945, *Ind. Journ. Phys.*, **19**, 159.
- STRATTON 1942, *ELECTROMAGNETIC THEORY*, p. 326.

83. ON THE CONDITIONS OF ESCAPE OF MICROWAVES OF RADIO-FREQUENCY RANGE FROM THE SUN

M. N. SAHA,* B. K. BANERJEA AND U. C. GUHA

(*Ind. Jour. Phys.*, **21**, 199, 1947)

(Received for publication, Sept. 15, 1947)

ABSTRACT

In this paper, we have discussed the conditions of escape of radio-frequency waves from the solar atmosphere with the aid of magneto-ionic theories of propagation of radio-waves through an ionised atmosphere traversed by a magnetic field. It has been shown from these theories that the magnetic field of the spots actually enables the *e*-component of the waves to escape from deeper layers of the solar atmosphere and thus provides an explanation of the observational fact that radio-waves are actually emitted by the spot regions themselves. It is shown that the same theories give a general and satisfactory explanation of all the facts observed so far, *e.g.*, the circular polarisation, and sudden intensification of emission with the onset of radio flares. Programmes for further work are indicated.

1. INTRODUCTION

In several communications to *Nature* and elsewhere, various British, Australian and New Zealander workers have described experiments which prove conclusively that during times of solar disturbance, there are large outbursts of radio-frequency energy from the sun. The wave-lengths of the radio waves, as observed by these workers, vary from 1.5 to 30 metres (200 Mc/sec to 10 Mc/sec) and there is short account of a solitary work in the centimetre region (Dicke and Beringer, 1946), in which emission has been measured by a different technique.

The communications are mostly short. The most complete account has so far been given by Appleton and Hey (1946). Relevant points from their account are given below.

The observations were made when there was outburst of sun-spot activity which started on 22nd February, 1946. According to their statement the sun-spot crossed the solar disc at a heliographic latitude 22°N, central meridian passage occurring on 28th February, 1946. The maximum size of the spot was some two thousand millionth part of the sun's hemisphere. A very extensive and brilliant solar flare occurred from approximately 12 hours to 15-03 hours on 28th February, and the accompanying radio fadeout which began just after 12 hours lasted till 20-0-0 hours. A great magnetic storm broke out with great activity at 7-22 hours on 2nd March. The days of greatest intensity of solar noise, *i.e.*, 27th and 28th February, occurred when the sun-spot was near the central meridian passage and at the time of intense sun-spot activity several solar flares were observed in addition to the most brilliant one to which reference has already been made. The sun-spot

decreased in size after the 28th February and at the same time solar noise subsided.

The reports so far published make it clear that the metre range microwave radiations are emitted only during times of solar activity. In fact a close statistical correspondence between the sun-spot activity and metre range micro-wave emission has been established by Pawsey, Payne-Scott and MacReady (1947) and others.

This close correspondence is further confirmed by the experiments of Ryle and Vonberg (1946) who, by an ingenious adaptation of the famous Michelson-Pease method of measuring stellar diameters, showed that the actual region from which these radio-waves are coming subtends an angle not greater than 10' of arc, the solar diameter being 32' of arc. The size of the radio-wave generating regions, thus determined, is of the same order of, though somewhat larger than, the size of the large sun-spot groups (3' of an arc). Pawsey *et al* find by a different method that the diameter is about 6'.

The main characteristics of these solar radio noise, as determined by the various workers, can be summarised as follows:—

(i) The radiation is closely connected with sun-spots, appearing and disappearing with the latter.

(ii) The radiation has the characteristics of random noise, the intensity of the spectrum is neither steady with time nor continuous in wave-length, nor monochromatic.

(iii) The intensity of radio-emission is extraordinarily high.—Appleton and Hey working on 4.7 metres, found that the radio flux from the active area was 10^3 times that associated with black body radiation from the disc as a whole. Supposing that only 1/200th part of the sun's

*Fellow of the Indian Physical Society.

hemisphere is active, the intensity increases to 2.10^5 times the black body radiation from the sun's disc.

(iv) The intensity is subject to sudden fluctuations occurring generally with the onset of flares or other disturbances.

(v) Polarisation.—Experiments on the polarisation of the radio noise have been carried out by Appleton and Hey (1946) in London, by Ryle and Vonberg (1946) in Cambridge and Martyn (1946) in Canberra. They have all found that the radio noise is invariably circularly polarised, but otherwise the descriptions are confusing. Describing the polarisation of waves from the sun-spot groups of July 27 to August 3, 1946, Ryle and Vonberg say:—

“Measurements taken over the period July 27 to August 3rd, showed the polarisation to be anticlockwise, viewed along the positive direction of propagation (left handed). Between August 3 and August 7, the degree of polarisation diminished, being virtually completely random on August 7. On August 8, 40% polarisation was observed again but with right-handed polarity, the result presumably of increased activity in a subsidiary sun-spot.”

Martyn (1946) working in the southern latitudes (35°S Canberra) while observing the same sun-spots occurring in the last week of July 1946 noted:—

“It was found that the right-handed circularly polarised power received was some seven times greater than that received when the system accepted only left-handed polarised radiation. Three days later, when this sun-spot group crossed the meridian these conditions were reversed; five times more power being then received on the left-handed than on the right-handed system”.

Thus simultaneously observing the same sun-spot groups the sense of rotation of the polarised signal in the two hemispheres were found by the observers to be opposite.

As will be made clear later, it will be helpful to the understanding of the phenomenon if, simultaneously with the recording of the polarisation, all the characteristics of sun-spots (heliographic latitude and longitude, distance from the centre of the disc, magnetic field strength, classification, etc.) are given.

Measurements for radiation below metre range

Appleton and Hey state that they could not detect any enhancement of solar noise on wave-lengths as short as 1/10 metre. Similar observations by the T.R.E. establishment on a 3/10 metre yielded a negative result. The radio noise associated with the sun-spot activity becomes significant, without very special technique, when the wave-lengths approach 1.5 metres. The results are in accordance with the observations of MacReady, Pawsey, Payne-Scott (1946). On the other hand Dicke and Beringer (1945) working in the centimetre range and using special technique found that microwaves of 1.25 cm. length are emitted during times of

solar activity, the corresponding black body temperature being 11000°K.

2. PRELIMINARY ATTEMPTS AT A THEORY OF THE PHENOMENON

The problem is to find out the physical mechanism which gives rise to the radio-frequency waves in the sun and also to discuss how these waves are propagated through the solar atmosphere. Let us first confine ourselves to the second aspect of the problem, for whatever may be the physical mechanism giving rise to the radio-waves, it is clear that their passage through the various layers of the solar atmosphere would be regulated by the laws of electromagnetism. As is well-known, the various layers of the solar atmosphere are highly ionised, the electron-density, according to well-tested astrophysical theories, being 10^{14} /c.c. for the photospheric level, 10^{12} /c.c. for the base of the chromosphere (500 km above photosphere) which fall to 3.5×10^8 /c.c. at the top of the chromosphere (14500 km). The density thereafter falls slowly throughout the whole corona, but is $\approx 10^3$ /c.c. even at distance of 10 solar diameters.

The quiescent sun has, like the Earth, a permanent magnetic field, the existence of which was first indicated by the investigations of G.E. Hale. On account of its small value, the reality of the effect has been sometimes called into question, but recent investigations by Thiessen (1946) appear to have satisfied the astrophysicists that the field is real. The value is 25 gauss at the solar magnetic equator, and 50 gauss at the magnetic poles. According to Hale and Thiessen the magnetic axis is inclined at an angle of 6° to the sun's axis, but for our purpose we can take the two axes to be identical. Besides this small permanent magnetic field, magnetic fields of a higher order are developed in spot regions during times of solar activity.

The conditions in the sun are, therefore, somewhat similar to those prevailing in the Earth's atmosphere (ionosphere) for transmission of radio-waves through it, and the same mathematical methods which have been developed by Appleton, Hartree and others, can be used in the present case.

The authors (Saha, Banerjea and Guha, 1947) have, however, completely recast the mathematical treatment of propagation of radio-waves through an ionised atmosphere which is traversed by a magnetic field, and results from this paper are freely used in the present one. The main conclusions of Appleton are, however, quite sufficient for a preliminary survey of the problem.

According to these workers, a beam of unpolarized radio-waves on entry into the ionosphere is split up into two waves, which are styled ordinary (shortly called o-wave), and extraordinary (shortly called e-wave). They travel with different velocities, i.e., refractive indices, have

different states of polarisation and are absorbed to different degrees. These quantities, *viz.*, the refractive indices, polarisation and absorption are functions of electron density N , damping, field-strength H , and θ , the angle of propagation which is the angle between the magnetic field and the direction of propagation. In the case when damping can be neglected the refractive indices for the two waves are functions of N , H , and θ and decrease steadily as N increases. When μ becomes zero, the wave can no longer proceed forward, but is reflected back. The limiting conditions (Appleton-conditions) for penetration are for the

$$\text{o-wave, } N < \frac{\pi m}{e^2} f^2 < 1.21 \times 10^{-8} f^2 \quad (2.1)$$

$$\text{e-wave, } N < \frac{\pi m}{e^2} f(f \pm f_h) < 1.21 \times 10^{-8} f(f \pm f_h). \quad (2.2)$$

where $f = \text{wave frequency} = c/\lambda$
 $f_h = \text{gyromagnetic frequency for a field } H$
 $= \frac{eH}{2\pi mc}$
 $= 2.8 \times 10^6 H$

These conditions are independent of θ .

Let us apply these conditions to the solar atmosphere.

For the o-wave,

$$N < 1.25 \times 10^{-8} \times f^2$$

$$\left. \begin{array}{l} < 1.25 \times 10^6 \text{ for } f = 10 \text{ Mc/sec, } \lambda = 30 \text{ m} \\ < 5 \times 10^8 \text{ for } f = 200 \text{ Mc/sec, } \lambda = 1.5 \text{ m} \end{array} \right\} \quad (2.1a)$$

This shows that the o-component of the metre waves cannot escape from the sun unless they originate in the corona, and that so progressively in the upper layers, as we take larger waves. The o-component of 30 metre waves can come only from beyond a distance of several diameters of the sun.

The e-wave should satisfy two conditions:

- (a) f should be $> f_h$
- (b) N should be $< 1.25 \times 10^{-8} \times f(f - f_h)$

(a) shows that the e-component of microwaves cannot escape from the quiescent sun unless $f > 100 \text{ Mc/sec}$, $\lambda < 3 \text{ metres}$, but microwaves of longer wave-length have been detected. (b) states that e-microwaves satisfying condition (a) would have to originate even in higher layers, *i.e.*, their probability of escape from deeper layers is much less than that of o-waves.

These difficulties have been sought to be explained with the aid of the hypothesis that the microwaves actually originate in the higher corona to which a temperature of the order of a million degree is ascribed. But the hypothesis does not explain why the microwaves are so copiously emitted during times of solar spottedness and are actually emitted, as now appears almost certain, from the spots

themselves and not from the quiescent regions, unless we make the very improbable assumption that it is only the spots which develop the million degree temperature. The assumption is extremely improbable in view of the fact that spectroscopic evidence shows that spots are regions of much lower temperature than even the photosphere. This necessitates the investigation of the problem from an altogether different point of view.

Sun-spots and microwave emission

The sun-spots, according to the classical investigations of Hale and Nicholson (1925), are found to show magnetic fields of entirely different order of magnitude than the quiescent sun, from a few hundred gauss for tiny spots to about 4000 gauss for the largest ones. Their direction is normal to the solar surface at the centre of the spot, but becomes inclined to the surface as we go outwards to the penumbral regions, as shown in Fig. 1. The largest number of spots occur in close pairs, showing opposite polarity, and and even those which are apparently single, appear to have an invisible companion, having opposite polarity somewhere inside the surface. In fact, the spots are known to be hydrodynamical vortices, passing underneath the apparent surface, the two ends of the vortices being the two components of the bifocal spots. Spot groups show very complicated forms for which reference may be made to original sources (Nicholson, 1938) and reports (Nicolet, 1942).

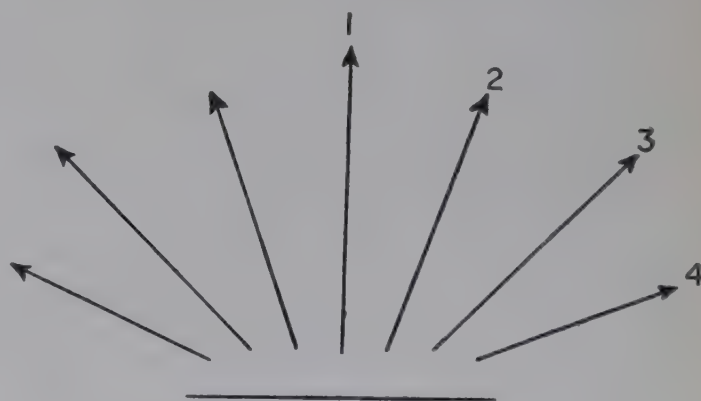


Fig. 1

Schematic representation of lines of force of the magnetic field in the region above a sun-spot (Nicholson).

Let us now apply the Appleton-conditions for escape of radio-waves from the spots, supposing that they originate somewhere within the spots.

For the o-component, since its condition of escape does not depend on the magnetic field, the conditions (2.1) will continue to apply, *i.e.*, the o-component of microwaves cannot escape from the sun, unless they originate in the corona over the spots.

We observe that $f_h = 2.8 \times 10^6 k$,

where k = value of the magnetic field in kilogausses: so that $\lambda_h = \frac{10.7}{k}$ cms. It is well known from Appleton's theory that the polarisation and refractive index of the e-component depend very largely on the quantity $\omega = f_h/f = \lambda/\lambda_h$. We have for the sunspots $\omega = 9.3km$, where m = length of the microwave emitted in metres. Taking $k=1$, $m=2.1$, $\omega \simeq 20$, but the value may be much larger for longer waves and larger fields. Taking an average value of 20 for ω , we can easily draw the following conclusions:

Since $\omega \gg 1$, the condition that the square of the refractive index vanishes at the point where the electron concentration is given by the formula $4\pi N e^2/m < p(p-p_h)$ is absent. If we plot the value of the refractive index for the e-wave in the case $\omega > 1$ as a function of electron concentration, we find that, when damping is neglected, the $(\mu_e^2 - N)$ curve is a smooth one, decreasing gradually to zero at $N = \frac{e^2}{\pi m} f(f+f_h)$ (vide Fig. 2), while μ_o^2 reaches the zero value at $N = \frac{e^2}{\pi m} f^2$.

Since the wave can proceed till this condition is satisfied the limiting concentration for escape of the e-wave is given by

$$N < 1.25 \times 10^{-8} f(f+f_h) \quad \dots \quad (2.3)$$

Taking $f = 1.5 \times 10^8$ ($\lambda = 2$ metres),

we should have $N \geq 1.25 \times 10^{-8} \times 1.5 \times 10^8 \times 2.8 \times 10^8$
 $\geq 6.6 \times 10^8 k$.

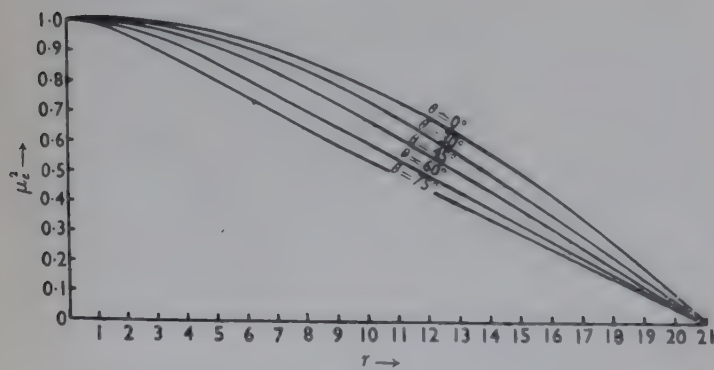


Fig. 2

Variation of the square of the refractive index of the extraordinary wave with electron concentration for different angles of propagation (for $\omega=20$).

The calculation shows that the e-component can come from far deeper layers than the o-component, in fact from deep chromospheric layers, where the electron density is $(1+\omega) \simeq 21$ times the limiting density for o-waves.

The magnetic field measured for the spots refer to the lowest layers—in fact, as will be shown later for the reversing layer of the spots. The field above and below must be very different. We have given in §3, plausible formulae for the

variation of the field above the reversing layer, and these formulae may probably be experimentally verified as suggested by Hale long ago (vide appendix).

But these methods are not applicable for finding out the value of the magnetic field below the reversing layer, for which we have to fall back upon some speculative theories. If the spots are hydrodynamical vortices, they should funnel out on reaching the chromosphere, but their cross-sections must be very small just below the reversing layer, and according to Chapman (1944), fields may reach enormous values of the order of a million gauss. If this be correct the e-component can escape from far deeper layers.

3. CHARACTERISTICS OF THE SPOT ATMOSPHERE

Though the ideas outlined in the previous paragraphs make it clear that it is the strong magnetic field of the sun-spots, which allows only one component of microwave beams to come out from very deep layers, the application of the above ideas to the actual problem of emission requires a more detailed knowledge of the physical conditions prevailing in various layers of the spot-region.

The physical quantities of which knowledge is particularly needed in this connection, are:

- (1) The concentration of different kinds of atoms and molecules at different levels.
- (2) The electron concentration at different levels.
- (3) The magnetic field and its variation with height.

Methods, based on sound physical theories, have been developed for determining the various physical characteristics of the normal solar atmosphere, with the aid of data obtained from astrophysical observations, account of which will be found in Unsöld's *Sternatmosphäre* and Stromgren's analysis of the composition of the solar atmosphere. The term "Solar atmosphere" is used in a comprehensive sense after Rosseland to denote the totality of the phenomena known under the terms: the Reversing Layer, the Chromosphere and the Corona, and they are treated together, because, inspite of the fact that the nomenclature had their origin in different groups of observational data, the problems of the three layers easily pass into one another.

It is well-known that the sun-spot and its neighbourhood show very great deviations from the normal solar atmosphere, marked by fall of temperature, development of magnetic fields, and radial, transverse and vertical motion of the solar gases, giving rise to difficult hydrodynamical problems. A comprehensive theory, explaining the whole history and physical characteristics of spots, is still wanting, but our requirements, as given above, are limited. But even here, information is very scanty. The elaborate methods, which have been used for finding out the concentration of various types of atoms and electron density of the normal solar atmosphere in different layers, can be

applied also to spots, but this has not yet been done. Only indirect methods of comparison with the normal atmosphere are available (Moore 1931, Richardson 1931). For these reasons, it is necessary to review critically the methods used for the normal solar atmosphere.

The normal reversing layer is a region extending from the level of the photosphere to the base of the chromosphere, a distance of 300-500 km. The Fraunhofer lines mostly originate from absorption of continuous photospheric light by the atoms and molecules contained in this layer.

Several methods are available for finding out the composition of the reversing layer, but the results, though of the same order, do not tally with each other. According to Russell (1928) the composition (percentage of atoms) is 91% H, probably 3% He, 3% O, 1.5% other elements of which Fe forms the preponderating part, and 1.5% electrons. The atmosphere is nearly purely hydrogen, and becomes more so as we ascend upwards. The total number of H-atoms over 1 c.c. of photosphere is given by Russell as 1.8×10^{23} /c.c.

The electrons in the reversing layers and the chromosphere are mostly derived from the thermal ionisation of metals.

For the chromosphere very extensive investigation by Wildt (1947), based on analysis of flash spectrum data, is available, from which Table I has been compiled:

TABLE I

Locality	Level above Photosphere	Hydrogen density	Electron density
Reversing layer	0 to 500 km	6.76×10^{15}	10^{14}
Base of chromosphere	500 km	4×10^{15}	1.6×10^{11}
Top of chromosphere	14,500 km	2×10^{10}	3.5×10^8
Corona	> 20,000 km		3×10^8 to 10^4

According to Wildt (1947) the concentration of H-atoms in the chromosphere is given by the formula:

$$n_H = 6.76 \times 10^{15} e^{-.92 \times 10^{-8} z} \text{ (in cms).}$$

The hydrostatic density gradient, on the assumption of a temperature of 5000°K is $6.9 \times 10^{-8} \text{ cm}^{-1}$. It is, as if the weight of hydrogen has diminished to $.92/6.9 = 1/7.5$ of its value or the temperature has risen to nearly 35000°K.

The electron-density at any point within the chromosphere can be obtained by extrapolation; assuming the exponential law to hold good, calculation shows that $n = n_0 e^{-\beta z}$ (in cms), where $\beta = .43 \times 10^{-8} \text{ cm}^{-1}$. The gradient is almost half that of H, as electrons are not obtained only from the ionisation of H but also from the metallic elements which are almost completely ionised.

The values of electron density in the corona (from 20,000

km upwards) are given by Bumbauch (1937). These are obtained from a thorough discussion of numerous measurements of the brightness of the corona, on the basis of K. Schwarzschild's hypothesis, generally accepted, that the continuous spectrum of the solar corona is due to photospheric light scattered by free electrons. Bumbauch's calculations (Unsöld, p. 440) extend from 20,000 km to nearly ten times the solar radius, and the density varies from 4×10^8 to nearly 10^5 /c.c. The figure for the top of the chromosphere (14,500 km) has been extrapolated by Wildt from Bumbauch's figure. Another calculation based on extrapolation of hydrogen densities, gives $n_e = 2 \times 10^{11}$ /c.c. at this height. Bumbauch's figures have recently been revised by Allen (1946) and van der Hulst (1947).

The magnetic field in the spot regions

Magnetic field of sun-spots has been systematically measured in the Mount Wilson Observatory since the great discovery by Hale in 1908, as part of the routine programme of the observatory and the results are available in publications of the observatory and in various reports.

For the measurement of the field, the iron line $\lambda = 6173.346 \text{ \AA}$, which is exceptionally sharp, has been generally used. As this is a line of intensity 5 on the Rowland scale, and in the chromosphere spectrum reaches only a height of 400 km, it can be taken that the fields measured refer to the lowest level of the spot.

But for the purposes of this paper, we require the value of the spot field at higher levels, and away from the axis of the field. There appears to be no systematic observation on this point, though Hale (1908) was aware of the necessity of such observations. He states:

"We have already seen that the strength of the field in spots apparently changes very rapidly along a solar radius, and is small at the upper level of the chromosphere."

We have given in Appendix the full passage from the original paper of Hale which suggests a programme for measurement of the magnetic field at various levels above the reversing layer of spots. To our knowledge these suggestions have not been worked out but they are worth a trial.

Two different and indirect methods, based on Mount Wilson measurement of the field over various distances from the centre of the umbra, are available. These are given below:—

(1) Broxon (1942) while observing the effect of the spot fields on cosmic rays suggested that the magnetic fields of unipolar spots may be fairly approximately represented by the field of a vertically placed magnet having a dipole moment $\mu = \sqrt{2} a H_0 / 8$ situated at a depth of $a/\sqrt{2}$ with the axis coinciding with the axis of the spot, where a = radius of the spot and H_0 is the field strength at the spot centre. For complete mapping of such a field, let A'SA be the plane of the spot and MS the axis of the spot, with the

dipole at M. We chose the frame-work XYZ, with X-axis along SA, Z-axis along MSM' and Y-axis perpendicular to the plane of the paper (Fig. 3). As the field is symmetrical

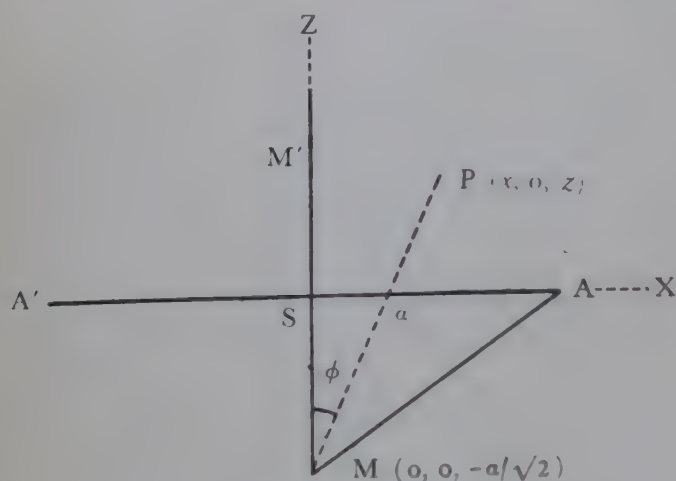


Fig. 3

The co-ordinate system for a circular spot (Broxon type)

about the axis let us find out the field at any point P $(x, 0, z)$ in the XZ plane. Let also $R = MP$ and $\phi = \angle PMS$ be the polar co-ordinates of P with M $(0, 0, -a/\sqrt{2})$ as origin.

Then the potential Ω at P is given by

$$\left. \begin{aligned} \Omega &= \frac{\mu \cos \phi}{R^2} = \mu \frac{(z + a/\sqrt{2})}{\{x^2 + (z + a/\sqrt{2})^2\}^{3/2}} \\ H_x &= -2 \frac{\mu \cos \phi}{R^3}; H_z = \frac{3\sqrt{2}}{8} H_0 \frac{\xi(\xi + 1/\sqrt{2})}{\{\xi^2 + (\xi + 1/\sqrt{2})^2\}^{3/2}} \\ H_\phi &= -\frac{\mu \sin \phi}{R^3}; H_\psi = \frac{H_0}{4\sqrt{2}} \frac{2(\xi + 1/\sqrt{2})^2 - \xi^2}{\{\xi^2 + (\xi + 1/\sqrt{2})^2\}^{3/2}} \\ H &= \frac{H_0}{4\sqrt{2}} \frac{\sqrt{\xi^2 + 4(\xi + 1/\sqrt{2})^2}}{\{\xi^2 + (\xi + 1/\sqrt{2})^2\}^{3/2}} = \frac{\mu}{R^3} \sqrt{1 + 3 \cos^2 \phi} \end{aligned} \right\} \quad (3.1)$$

with $x = a\xi, \quad z = a\zeta.$

Since in the above co-ordinate systems,

$$\left. \begin{aligned} \tan \phi &= x/(z + a/\sqrt{2}) = \frac{\xi\sqrt{2}}{(1 + \xi\sqrt{2})} \\ \text{we have } \cot \psi &= H_z/H_x = \cot \phi - \frac{1}{3 \sin \phi \cos \phi} \end{aligned} \right\} \quad (3.2)$$

Expression (3.1) gives the magnitude of the magnetic field at any point on or above the spot and to get field direction, we plot the curves representing lines of force given by

$$R = A \sin^2 \phi, \quad A = \text{arbitrary constant.}$$

To show how the field intensity varies with distance from the spot centre and with height, the quantity H/H_0 has been plotted (Fig. 4) against ξ for values of $\zeta = 0, .1, .5, .6, 1.0$. The topmost curve for $\zeta = 0$ gives H at different points along the spot surface. At the edge of the spot H/H_0 becomes

nearly 14% whereas it ought to be zero. The other curves for $\zeta = .1, .3, .6$ and 1.0 give the field intensities at different points on planes parallel to the spot surface at heights of

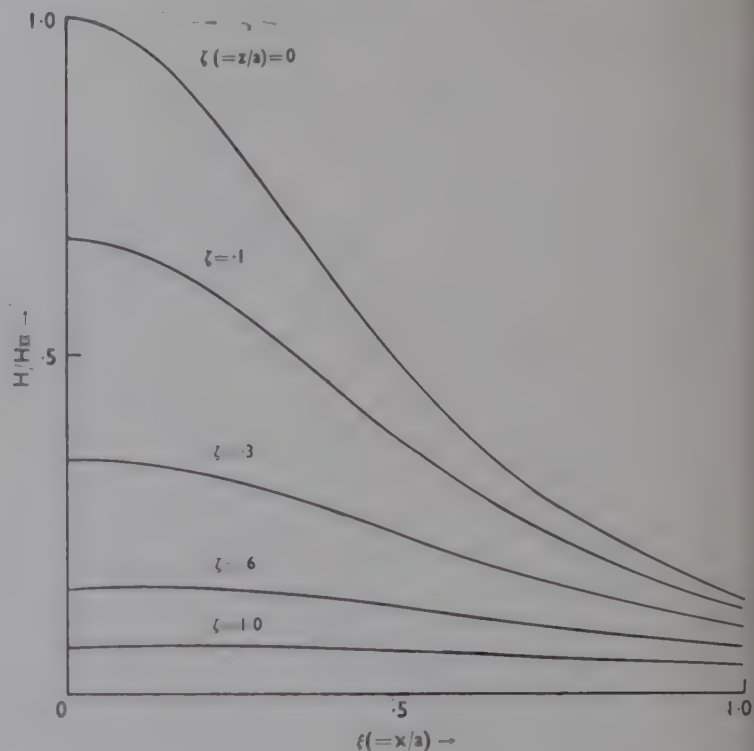


Fig. 4

Variation of the intensity of the magnetic field along and above the spot surface (Broxon type).

$\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{6}}$ and unit times the spot radius. As we go higher and higher above the spot surface, the field becomes more or less constant over the entire plane as is evident from the lowest curve for $\zeta = 1$, which is situated at a height equal to the spot radius.

Fig. 5 gives the lines of force at different points. The tangent to these curves at any point gives the direction of the magnetic field at that point. The thick line SA is the spot surface. From (3.2) we note that ϕ -constant lines are the lines of constant ψ . Values of ψ for certain different values of ϕ are represented by arrows in the diagram. $\psi = 0$ is the line coinciding with the central line $\phi = 0$. Gradually as ϕ increases, ψ also increases, and at the periphery $\psi = \pi/2$, showing that the z-component of the magnetic field is absent at the edges, i.e., the field is perfectly horizontal at the edges.

(2) Chapman (1943) has given another approach to the problem. For finding out the spot fields at different points, he argues as follows:

"If the two ends, whether of the straight or semicircular magnet, are sufficiently far apart, we can calculate the magnetic field near each as if the others were not there. Suppose the surface density σ (of magnetic poles) over the end depends only on the distance r from the centre of the spot; and the magnetic intensity H and its inclination

ψ , will likewise depend only on r . I have calculated ψ for various relationship between σ and r in order to find out what distribution of σ would agree approximately with Nicholson's measurement of ψ for a sun-spot. The details

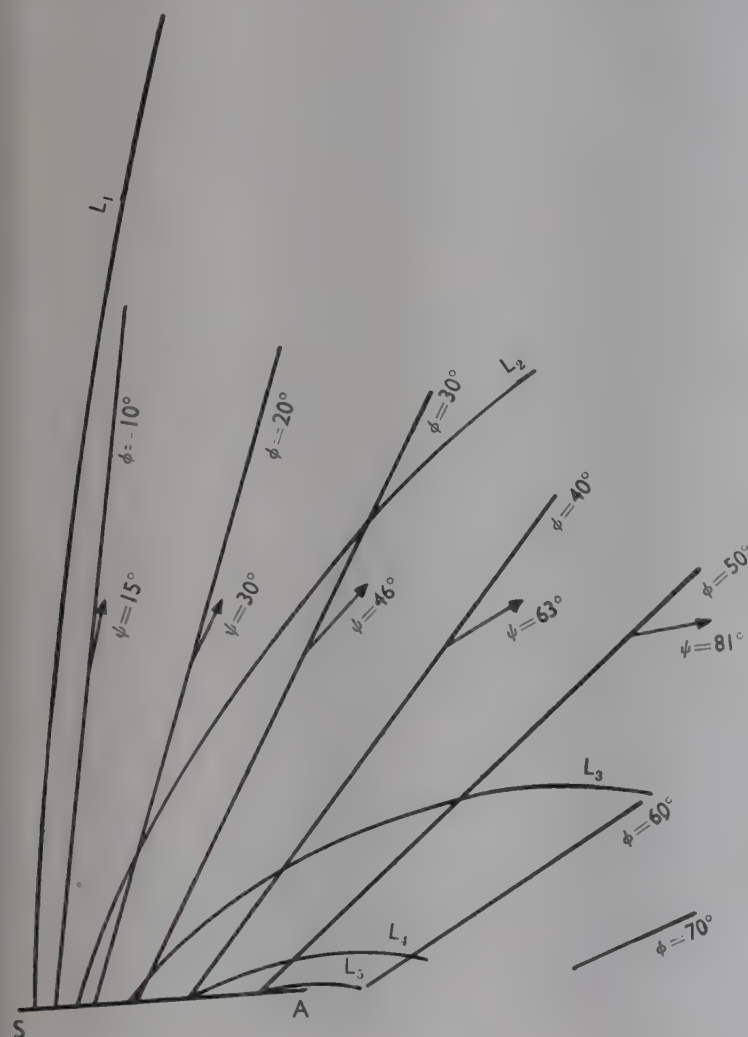


Fig. 5

Lines of force of the spot field according to Broxon.

are omitted here. I give only the results for the assumed variation of surface density,

$$\sigma = \frac{H_0}{2\pi} \left(1 - \frac{r^2}{a^2} \right)^2 \quad \dots \quad (3.3)$$

Taking the same axes as before, the magnetic potential at a point P (x, o, z) is given by

$$\Omega = \frac{H_0 a}{2\pi} \int_0^1 \int_0^{2\pi} \frac{\rho d\rho d\phi}{\sqrt{\lambda^2 - 2\lambda\rho \cos \phi \cos \psi + \rho^2}}, \quad (3.4)$$

where $\lambda^2 = \frac{x^2 + z^2}{a^2}$, $\tan \psi = \frac{x}{z}$, $r/a = \rho$.

This is an elliptic function in λ .

Since for our purpose of investigating the propagation of e.m. waves in the solar atmosphere, we are not much

concerned with the actual variation of the field over the surface of the spot, but mainly with the order of magnitude of H on and above the spot and as our line of argument will be the same for different kinds of variations of the magnetic fields, we do not proceed further with Chapman's

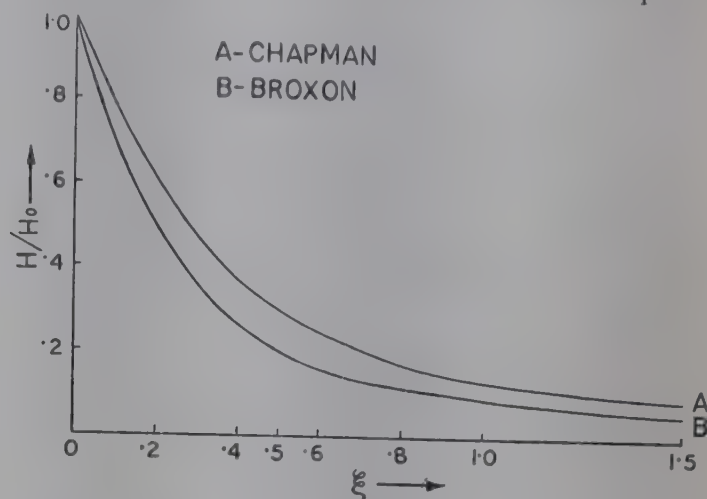


Fig. 6

Variation of the value of the magnetic field along the axis of a spot according to Chapman (A) and Broxon (B). ($\xi = z/a$, z =distance along the axis, a =radius of spot).

assumptions, but stop here merely comparing the variation of H for the axial case for Chapman and Broxon fields. For the axial case expression (3.4) gives

$$H_z = \frac{H_0}{3} \cdot \{ (8\xi^4 + 12\xi^2 + 3) - 8\xi(1 + \xi^2)^{\frac{3}{2}} \} \quad \dots \quad (3.5)$$

Values of H/H_0 have been plotted against ξ for $\xi=0$ (axial case) for Chapman fields (A) and Broxon fields (B) in Fig. 6. The general trend of the two curves is the same, but Chapman's values are somewhat higher. We find that in both the cases, for large spots of radius $a=28,000$ km, and $H_0=3600$ Γ , large fields of the order of 1000 Γ persist at heights of the order of 15,000 km, i.e., the top of the chromosphere. For such spots the fields reduce to approximately 13 to 10% at 30,000 km.

4. PROPAGATION OF E.M. WAVES

We are now in a position to discuss the actual problem of propagation of radio-waves through the solar atmosphere surrounding the spots, on the supposition that these waves have their origin deep within the spots, and are consequent on the physical processes taking place within the sun which give rise to spots.

As mentioned before, the propagation depends on: N, the electron density, H, the magnetic field, δ the damping coefficient $= \nu/p$ where ν is the number of collisions suffered by an electron per sec, p =pulsatance $= 2\pi f$, θ the angle of propagation, which is the angle between the direction of propagation and the positive direction of lines of force.

We have discussed N and H, we shall now discuss the other quantities.

(a) The damping factor $\delta = \nu/p$

In the reversing layer (500 kms), we have $T \simeq 6000^\circ\text{K}$, n = concentration of atoms mostly hydrogen $= 4 \cdot 10^{15}/\text{c.c.}$, n_e = electron density $\simeq 10^{14}$ per c.c. The mean free path of electrons is, therefore, $L_e = 4\sqrt{2} L$, where L is the mean free path of heavy particles.

$$\text{Hence } L_e = 4\sqrt{2} \frac{1}{\sqrt{2} \pi n \sigma^2} = \frac{4}{\pi \cdot 4 \cdot 10^{15} \cdot 10^{-16}} \simeq 3 \text{ cms.}$$

$\bar{v}$ = mean molecular velocity of electrons

$$= \sqrt{\frac{3kT}{m_e}} \simeq 5 \cdot 10^7 \text{ cms.}$$

$$\text{Hence } \nu = \bar{v}/L_e \simeq 2 \cdot 10^7 \text{ sec}^{-1}.$$

$$\text{Taking } \lambda = 2m, f = 1 \cdot 5 \cdot 10^8, p = 2\pi f$$

$$\text{and } \delta = \nu/p \simeq 2 \cdot 10^{-3}.$$

The value of δ is thus seen to be very small even on the reversing layer. In the higher layers δ falls very rapidly and therefore it is justifiable to neglect damping altogether.

(b) The angle of propagation

Let the globe represent the sun, C its body centre and CE the direction of the Earth. E is the centre of the visible disc. Let S be the position of the centre of the umbra of the spot.

Then the direction of the spot axis, and of the central magnetic field of the spot is along CS. The angle ECS,

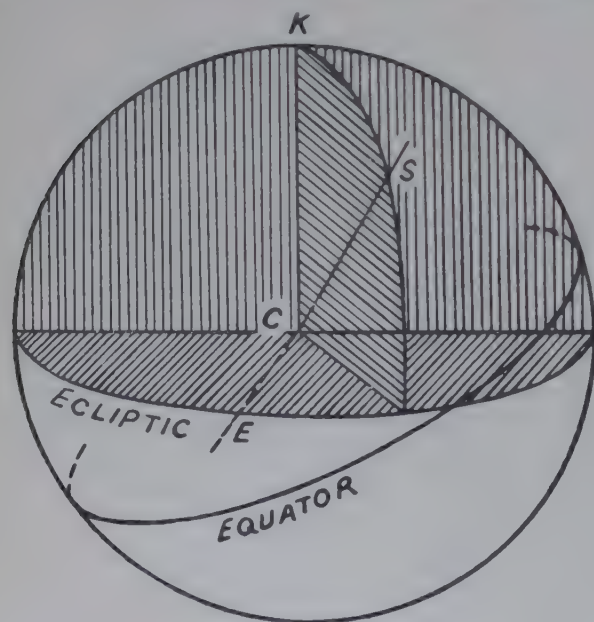


Fig. 7

Position of spot as seen from the earth. S-position of the spot on sun (after Smart, *Spherical Astronomy*).

which is generally denoted by ρ (but we shall denote it by χ as ρ has been used in a different sense), can be obtained by calculation from daily observation of the spot (*vide* Smart, *Spherical Astronomy*, p. 172). When the spot first appears on the east limb, $\chi = 90^\circ$, but there is hardly any observation available at the first appearance of the spot. Observations generally start after a day, when $\chi \simeq 75^\circ$ then gradually χ diminishes day by day, but even during central meridian passage χ is generally different from zero, except on very rare occasions. After central meridian passage, χ again increases day by day till it is 90° when the spot disappears on the west limb.

Choice of Axes—The plane ECS may be taken as the (XZ) plane, CE being the axis of Z, the axis of X being perpendicular to CE in the plane ECS. The axis of Y is perpendicular to the plane of ECS (Fig. 8).

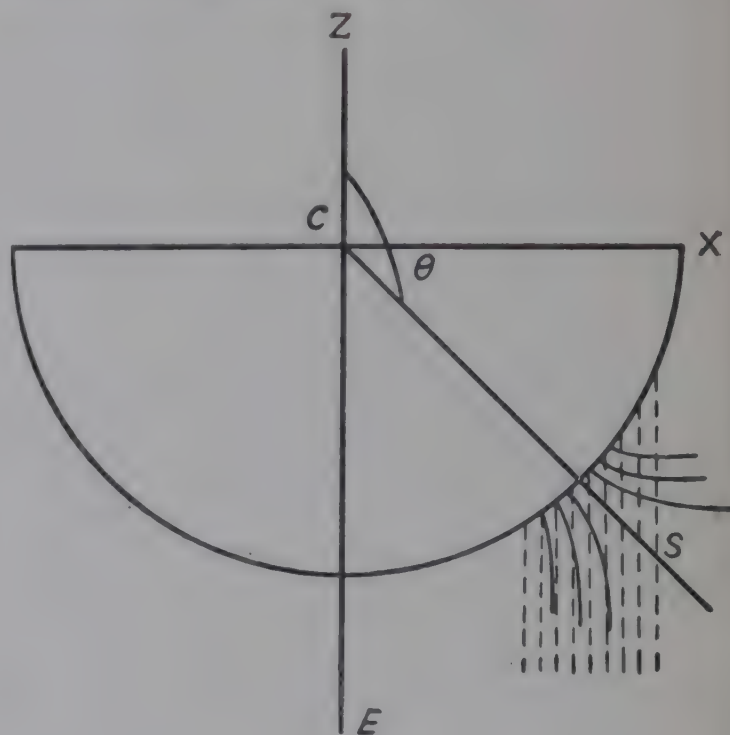


Fig. 8

Plane through Earth, Sun's centre and spot centre, showing how angle of propagation of waves varies in the neighbourhood of spot.

Angle of propagation—(See Fig. 8) According to our assumption, the source of radio-waves is the funnel shaped volume about S, with CS as axis. The volume comprises the whole conical space of the solar atmosphere with the spot as the base, which is traversed by the lines of force. If the lines of force were everywhere parallel to CS, $\theta = \chi$ if the polarity of the spot were R (lines of force away from the surface) and $= |\pi - \chi|$ if the polarity were V (lines of force passing into the surface).

But such is not the case, as the lines of force curve away from the direction of CS, as discussed in § 3. Let us find out the angle θ for any point P ($a\xi, a\eta, a\zeta$) within the spot.

This is the angle between CE, and the tangent to the lines of force at P. These make an angle ψ defined by (3.2) with CS, at an azimuth $\alpha = \tan^{-1} \eta/\xi$.

θ varies between $\chi + \psi$, $\chi - \psi$ as α varies between 0 and 2π .

The equations of propagation of the radio-waves through the spot atmosphere can now be written, using the symbols of the previous paper. They are:

$$\left. \begin{aligned} \frac{d^2}{du^2} (E_x + iF_1 E_y) + q_0^2 (E_x + iF_1 E_y) &= 0 \\ \text{for the o-wave,} \\ \text{and } \frac{d^2}{du^2} (E_x + iF_2 E_y) + q_e^2 (E_x + iF_2 E_y) &= 0 \\ \text{for the e-wave,} \end{aligned} \right\} \quad (4.1)$$

where $u = 2\pi z/\lambda$, $F_1 = \sqrt{1+g^2} - |g|$, $F_2 = \sqrt{1+g^2} + |g|$,
 $g = \omega \sin 2\theta/2 \cos \theta (r-1)$

$$\left. \begin{aligned} q_0^2 &= 1 - \frac{r}{1 + \omega \sin \theta (\sqrt{1+g^2} - |g|)} \text{ for } r < 1 \\ &= 1 - \frac{r}{1 - \omega \sin \theta (\sqrt{1+g^2} - |g|)} \text{ for } r > 1 \end{aligned} \right\} \quad (4.2)$$

$$\left. \begin{aligned} q_e^2 &= 1 - \frac{r}{1 - \omega \sin \theta (\sqrt{1+g^2} + |g|)} \text{ for } r < 1 \\ &= 1 - \frac{r}{1 + \omega \sin \theta (\sqrt{1+g^2} + |g|)} \text{ for } r > 1 \end{aligned} \right\} \quad (4.8)$$

The waves will be able to come out as long as q_0^2 and q_e^2 are > 0 . Let us first investigate the probable values of q_0^2 and q_e^2 in the spot region. They vary from point to point and we give the values of the relevant quantities for $\lambda = 1.5m$, $f = 2 \cdot 10^8/\text{sec}$.

We have $N_0 = \frac{mp^2}{4\pi e^2} = 5 \cdot 10^8$, $\omega = 1.4 \times 10^{-2}$ H.

Reference to paper (I)* shows that whatever the values of ω and θ , q_0^2 always tends to zero at $r=1$. This happens at a height of 13,500 km. So all o-waves coming from below this height are turned back.

As regards the e-wave, the transparency extends to the point where $r=1+\omega$. For the present case, we assume that N , the ion-concentration varies according to the law $N = N_0 e^{-\beta z}$ (vide Table II). The e-wave can leak out from levels where $r \leq 1+\omega$. For the present case this happens at $z > 3900$ kms. So the whole column, above a height of 3900 km, would be transparent to the e-waves of wave-length 2m (Fig. 9).

It is easy to see that the shorter waves would be able to come from correspondingly deeper layers.

Polarisation and sense of polarisation of the waves—Detailed description of measurements of polarisation is not available; but in all the short notes which have been published

it is stated that the polarisation is circular, even when the spots are close to the limb. Some state that the sense of polarisation changes on crossing the meridian (Martyn, 1946), while others do not find any such change (Bowen, 1946).

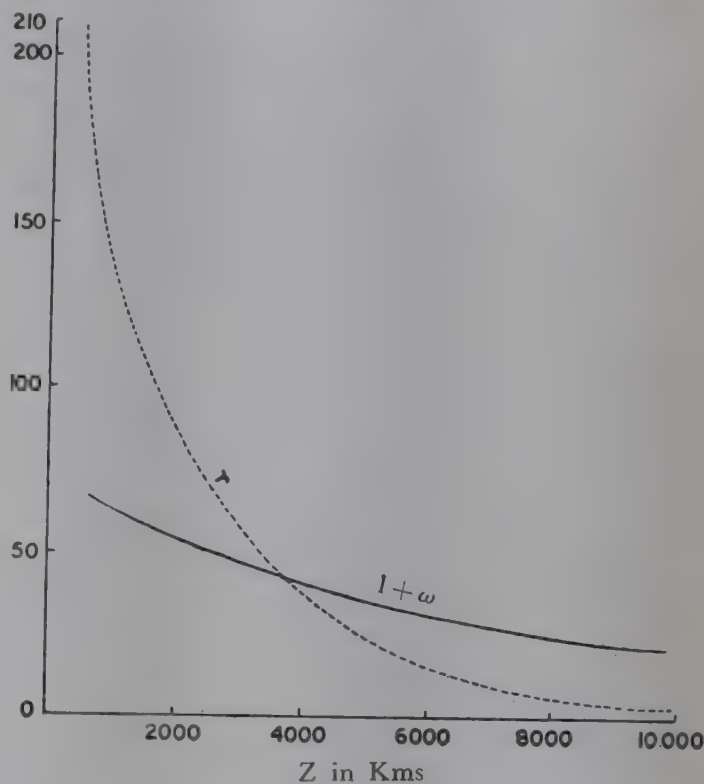


Fig. 9

The dotted curve shows the variation of $r = \frac{4\pi N e^2}{m p^2}$ with height over the spot for $\lambda = 2m$. The other curve gives $(1+\omega)$ as a function of height.

It is only possible to make some general statements about polarisation from our theory. We have $H_y/H_x = \sqrt{1+g^2} - |g|$ both for the o-wave, and the e-wave. Since g is changing at every point, so polarisation of the wave, as it is propagated through the solar atmosphere, is constantly changing. A large $|g|$ means "linear polarisation", a small $|g|$ means circular polarisation. Inside the chromosphere $|g|$ is large, hence the waves will be "linearly polarised". But as the waves pass through the corona both ω and r tend to vanish and $\omega \sin^2 \theta/2(r-1) \cos \theta$ is a very small quantity, e.g., it is 0.066 for $\theta = 120^\circ$ at a height of 10^6 km above the photosphere and hence $r \rightarrow 1$, and the waves become circular. Table II gives the values of r and ω for the spot atmosphere at various heights.

The sense of polarisation would depend upon the value of θ .

The waves have to pass through the Earth's ionosphere before we receive them. But in this case

$$r = \frac{4\pi N e^2}{m p^2} = \frac{N}{5 \cdot 10^8} \simeq 10^{-2}, \quad \omega = f_h/f = 7 \times 10^{-2},$$

$$g = 0.0035 \cos^2 \theta \simeq 0.$$

*Saha, Banerjee and Guha, 1947, *Ind. J. Phys.*, 21, 181.

TABLE II

Level above photosphere in km	N_e	(r)		H (Broxon)	ω
		Normal Atmos- phere	Spot Atmos- phere		
0	$1.6.10^{11}$ cc.	320	176	3600Γ	50.4
500	$1.29.10^{11}$ „	258	141.9	3330 „	46.6
1,000	$1.04.10^{11}$ „	208	114.4	3063 „	42.9
1,500	$8.37.10^{10}$ „	167	91.85	2885 „	40.39
2,000	$6.80.10^{10}$ „	136	74.80	2720 „	38.8
3,000	$4.42.10^{10}$ „	88	48.40	2364 „	35.10
5,000	$1.86.10^{10}$ „	37	20.35	1830 „	25.62
8,000	$5.12.10^9$ „	10	5.50	1296 „	18.14
10,000	$2.14.10^9$ „	5	2.75	1068 „	15.00
14,500*	3.10^9 „	.66	.53	720 „	10.80
20,000 ¹	$2.9.10^9$ „	.64	.35	18 „	8.65
30,000	$2.5.10^9$ „	.50	.28	360 „	5.04
40,000	$2.1.10^9$ „	.46	.25	187 „	2.62
50,000	$1.7.10^9$ „	.34	.19	104 „	1.46
100,000	$.85.10^9$ „	.20	.11	14 „	.20
1000,000	$.11.10^9$ „	.00	.00	0	0

*This value is not extrapolated from the curve $n=n_0e^{-z}$, but is an experimental value obtained from coronal data.

(1) These values are taken from extrapolation of the values of electron concentration in the corona obtained from scattering of light by free electrons given by Bambauch (See Physik der Stern-atmosphäre, page 440, 1938) and recently corrected by Allen (1946), and Van de Hulst (1947).

Hence $F_1=F_2=1$, i.e., the magnetic field is too weak to cause any change in the polarisation of the micro-waves from the sun.

5. GENERAL DEDUCTIONS

It is not possible to penetrate more deeply into the phenomena with the aid of our theory, unless the observations become more refined and the technique is improved, but some general statements can be made.

The equations of propagation show that the escape of waves and the sense of their circular polarisation are extremely sensitive to the value of the spot field and the concentration of electrons. In our treatment we have taken the source to be single spot (α -type), but observations have shown that majority of spots are bipolar, consisting of a leader and a follower with opposite polarity, whose field-strength undergoes rapid changes with the age.

Let us quote from Chapman (1943):

“Sun-spot Dipole Moments.—Hale found that most sun-spot groups at some stage in their life-history, show bipolarity that is to say, they include two spots, or two regions or groups of spots, of opposite magnetic polarity, one red (R) and the other violet (V). At other stages, however, there is often only one spot, of like polarity over all its area; this is called a unipolar spot.

A typical spot group begins as two small spots, or two groups of spots, of opposite polarity, nearly in the same latitude, and 3° or 4° apart in longitude. The two principal spots grow rapidly and separate in longitude to a distance of 10° or more; the rear spot attains its maximum area in 3 or 4 days; the leader attains a larger maximum area in 7, 8 or 9 days, many smaller spots develop within the group, mostly near the two main ones. The dipole moment of the group is greatest when the spots are largest and furthest apart.

Consider a notable case, that of the great bipolar group M. W. 6725, 8° S, consisting of two great spots each of radius 20,000 km, about 14° apart, together with many smaller spots between; for this group $H=3900\Gamma$; considering only the two large spots, the dipole moment is $5 \times 10^{18} \text{ km}^3$, i.e., 60,000 times as great as the Earth's dipole moment, and about $1/170$ of that of the sun. The sun-spot dipole moment is of course horizontal, and nearly parallel to the sun's equator, though the leading spot is generally somewhat nearer to the equator than is the follower. At the equator the dipole axis is along the equator, and according to W. Brunner its inclination to the equator increases with latitude to about 16° at 30° latitude.”

Many of the spots whose radio emission had been under investigation during the last and the present year, appear to have been of this type.

In such cases, each one of the component spots with different polarity will emit microwaves of different intensity and with circular polarisation of opposite sense. Though the waves from each spot may be co-herent, the waves from the two spots may not be co-herent, like light from two distinct sources. This appears to explain in a general way the observations of Ryle and Vonberg, Martyn, and of Appleton and Hey. But it is desirable that radio observations be coupled with simultaneous observations of the polarity and field strength of the component spots.

When the spot group is of the γ -type (multipolar and without demarcation) the polarisation may be random.

Sudden changes in intensity.—Sudden changes in intensity are expected when H and N change suddenly. This happens during flares which, as Geovanelli (1945) has shown, are connected with the γ -type of spots, where the field strength undergoes rapid changes. This may affect microwave emission in two ways, (1) sudden increase in the value of H, will allow the e-component of the microwave to come from deeper layers and vice

versa, (2) if the physical mechanism of emission given out by the senior author (Saha, 1946) be correct, sudden fluctuations of magnetic field will induce more copious emission of microwaves. But this point requires further investigation.

APPENDIX 1

The line $\lambda=6173.346$ is the weakest member of a $d^7p^5D-d^7p^5P$ multiplet of Fe. Its position is given in table mentioned below:

The multiplet is $d^7s^5D-d^7s^5P$ according to Russell. The excitation potential of the 5D_0 level is 4.21 volts ($\nu=34121 \text{ cm}^{-1}$). The other lines of the multiplet, notably 6137.005, and 6151.630 etc, are also sometimes used for measurement of the sun-spot fields.

The theoretical Zeemann-pattern of 6173.32 is given by $\Delta\nu=\pm a(o, 5/2)$.

This is also experimentally verified. The Mount Wilson values of magnetic field are obtained from comparison of laboratory data with observational data, and are therefore independent of particular Zeemann-pattern.

	5D_0	5D_1	5D_2	5D_3	5D_4
5P_1	1 6173.346 16194.19 (400)	5 6213.44 16089.79 (500)	5 6297.83 15874.16 (500)		
5P_2		1 6137.005 16290.09 (200)	6 6219.190 16074.59 (500)	10 6335.34 15780.11 (500)	
5P_3			1 6151.630 16251.35 (350)	6 6265.145 15956.92 (500)	10 6430.86 15543.73 (800)

Hale's suggestion for measurement of magnetic field in the higher layers of the spot

"On considerations it will be seen, however, that the separation of the doublets must depend, in some degree on the distribution of the absorbing vapor in the solar atmosphere, and on the coefficient of absorption of the particular line employed. A striking instance of this kind, affecting lines of the same series, is illustrated in the case of hydrogen, described in a previous paper.¹ Although the H_α line extends to the upper part of the chromosphere and prominences, the mean level represented by its absorption is much lower than that given by H_α . The consequence is that H_α enables us to photograph the solar vortices, the

characteristic stream lines of which do not appear at the lower H_α level. Similarly, if the intensity of a given titanium line falls off rapidly, the level represented by this line may be comparatively low. If, on the other hand, its intensity curve is of such a form as to indicate that the absorption at higher elevations plays an important part, the mean level represented by the line may be considerably higher than in the previous case. To settle this question we must know:

- (1) The range of elevation in the spot of the vapors of iron, titanium, and other elements;
- (2) The intensities of the lines of these elements at different levels;
- (3) The rate at which the strength of the field decreases upward.

In the absence of information regarding the first two points, we may enquire as to the probable relative behavior of titanium, iron, and other elements if the distribution of the vapors at different levels were the same as in the chromosphere. From a discussion of a large number of photographs of the flash spectrum, made by different observers at several eclipses, Jewell has compiled a table showing the heights above the sun's limb attained by various lines in the blue and violet.² The heights for titanium range from 100 miles (160 km) for 4466.0 to 3500 miles (5640 km) for 4466.7, while certain strong enhanced lines in the ultra-violet reach elevations of 6000 or 8000 miles (9660 or 12,880 km). For iron the minimum height is 200 miles (320 km) for 4482.4 and the maximum 1000 miles (1610 km) for 4584.0. Chromium ranges from 100 miles for 4280.2 to 1200 miles (1930 km) for 4275.0; manganese from '100 miles or more' for 4451.8 to '800 miles (1290 km) or more' for 4030.9; vanadium from 100 miles for 4390.1 to 200 miles for 4379.4. It thus appears that the range in level represented by the titanium lines is much greater than for the lines of iron, chromium, manganese, and vanadium. If the vapors were similarly distributed in spots, the maximum strength of field indicated by the titanium lines should therefore correspond with the maximum value for iron, but some titanium lines, produced by absorption at higher mean levels, should give lower field strength. Chromium should agree more nearly with iron. Vanadium, if the less refrangible lines reach no greater elevations, should give closely accordant (maximum) values for the field strength. It will perhaps be possible, with the aid of the 30 feet spectrograph, to determine the relative levels in the chromosphere attained by most of the lines in question, but it is a much more difficult matter to do this for sun-spots. I hope, however, that our new spectroheliograph of 30 feet focal length may throw some light on this subject."

² "Total Solar Eclipses of May, 28, 1900, and May 17, 1901." Publications of the U.S. Naval Observatory Series, Vol. IV, Appendix 1.

¹ Solar Vortices.

It is evident that these considerations will have no bearing on the present problem unless the field strength decreases very rapidly upward in spots. That this probably occurs is shown by the fact that the D-lines of sodium and the b-lines of magnesium are usually but slightly affected in the spot spectrum,³ and are displaced through a very small distance when the Nicol is rotated. Thus, at the level represented by these lines, which attain elevations in the chromosphere probably not exceeding 5000 miles, the field strength is reduced to a small fraction of its maximum value.

ACKNOWLEDGMENT

Two of us, B. K. Banerjee and U. C. Guha have been the recipients of two Research Scholarships from the Radio Research Committee of the Council of Scientific & Industrial Research (India) and wish to express their thanks to the Council for facility to work and permission to publish this paper.

Palit Laboratory of Physics,
Calcutta University.

³ Except for the strengthening of the wings, which may be produced by some cause other than a magnetic field.

REFERENCES

- ALLEN, 1946, *M.N.R.A.S.*, **106**, 137.
 APPLETON and HEY, 1946, *Phil. Mag.*, **37**, 73.
 BROXON, 1942, *Phy. Rev.*, **62**, 521.
 BUMBAUGH, 1937, *A. N.*, 263.
 CHAPMAN, 1943, *M.N.R.A.S.*, **103**, 117.
 DICKE and BERRINGER, 1946, *Astro. Journ.*, **103**, 76.
 GEO-VANELLI, 1946, *Nature*, **158**, 87.
 HALE and NICHOLSON, 1925, Magnetic observations of Sun's spots.
 HALE, 1935, *Nature*, **36**, 703.
 HARTREE, 1931, *Proc. Camb. Phil. Soc.*, **27**, 143.
 HULST, 1947, *Astro. Journ.*, **105**, 431.
 PAWSEY, MACREADY and PAYNE-SCOTT, 1946, *Nature*, **157**, 158.
 PAWSEY, MACREADY and PAYNE-SCOTT, 1947, *Proc. Roy. Soc.*, **190**, 357.
 MARTYN, 1946, *Nature*, **158**, 308.
 MOORE, 1931, *Astro. Journ.*, **75**, 222, 298.
 NICHOLSON, 1926, *Pub. Ast. Soc. Pac.*, **38**, 347.
 NICOLET, LE SOLEIL, page 51, fig. 30.
 RICHARDSON, 1931, *Astro. Journ.*, **73**, 216.
 RUSSELL, 1929, *Astro. Journ.*, **70**, 11.
 RUSSELL, 1934, *Astro. Journ.*, **78**, 239.
 RYLE and VONBERG, 1946, *Nature*, **158**, 339.
 SAHA, 1946, *Nature*, **158**, 717.
 SAHA, BANERJEE and GUHA, 1947, *Ind. J. Phys.*, **21**, 181.
 THIESSEN 1946, *Ann. de Astro. Phys.*, **9**, 101.
 WILDT, 1947, *Astro. Journ.*, **105**, 43.

84. NOTE ON DIRAC'S THEORY OF MAGNETIC POLES

(*Phys. Rev.*, **95**, 1968, 1949)

In a note bearing the above heading, Professor H. A. Wilson¹ has described a simple method for finding out the value of Dirac's free magnetic poles. I may point out that this method was described by me nearly thirteen years ago² in a paper "On the origin of mass in neutrons and protons." I may just quote the result:

"It was Dirac who first showed that quantum mechanics demands the existence of free magnetic poles, having the

pole strength (or magnetic charge) $ch/4\pi e = e/2\alpha$, where α = Sommerfeld fine-structure constant. Recently, the present author deduced the existence of free magnetic poles from very simple considerations. If we take a point charge e at A and a magnetic pole μ at B , classical electrodynamics tells us that the angular momentum of the system about

$A-B$

the line AB is just $e\mu/c$. Hence following the quantum logic, if we put this $= \frac{1}{2} \cdot h/2\pi$, the fundamental unit of angular momentum, we have $\mu = ch/4\pi e = e/2\alpha$ which is just the result obtained by Dirac."

¹ H. A. Wilson, *Phys. Rev.* **75**, 308 (1949).

² *Ind. J. Phys.* **10**, 145 (1936).

85. VERTICAL PROPAGATION OF ELECTROMAGNETIC WAVES IN THE IONOSPHERE

M. N. SAHA, B. K. BANERJEA, AND U. C. GUHA

(*Proc. Nat. Inst. Sci. Ind.*, **17**, 205, 1951)

(Received November 15, 1950; read January 1, 1951)

SUMMARY

A connected discussion of the equations for the vertical propagation of e.m. waves in the ionosphere is given in standardised notation. It is shown that the electric field vector components E_x and E_y are coupled by polarisation terms, ρ_1, ρ_2 which are functions of G. M. latitude and height; and the propagation vectors, V and W , equal respectively to $(E_x + i\rho E_y)/\sqrt{1+\rho^2}$, for two values of ρ , are governed by two refractive indices q_0, q_e , and a coupling term ϕ ; V and W may be identified with o - and e - waves respectively. The five quantities needed to define wave propagation completely are $\rho_1, \rho_2, \phi, q_0$ and q_e ; we have given a detailed discussion of the first three, and have omitted discussions about q_0 and q_e which are identical with those given by Appleton and have been discussed in detail by Booker (1935) and others. It is shown that the coupling term ϕ can be neglected everywhere for F -layer propagation except very near the G.M. poles, while the E -layer propagation is more difficult to handle.

INTRODUCTION

Wave equations for the propagation of e.m. waves in the ionosphere had been given by Hartree (1929), Epstein (1930), Försterling (1931), Saha and Rai (1937), Rawer (1939), and Rydbeck (1940) and more recently by B. K. Banerjea (1947). Most of the older investigations were confined to the particular case of vertical propagation in the magnetic equator or poles. In recent years vertical propagation in any latitude has been tackled by Rydbeck (1941) and by Saha, Banerjea, Guha (1947), but a full discussion of the equations is still wanting. We discuss here the exact equations from a standpoint which is likely to throw light on the nature of modification of wave propagation at high geomagnetic latitudes.

§1. DEDUCTION OF EQUATIONS OF WAVE PROPAGATION

The deduction of the equations of propagation of e.m. waves in the ionosphere follows from the usual method

of e.m. theory of light. We start with the Maxwell's equations:

$$\begin{aligned}\nabla \times \mathbf{H} &= \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}; \quad \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} \\ \nabla \cdot \mathbf{D} &= 0; \quad \nabla \cdot \mathbf{H} = 0; \quad \mathbf{D} = \mathbf{E} + \mathbf{P} = \mathbf{K} \cdot \mathbf{E}.\end{aligned}\quad (1.1)$$

It will be presently shown that the dielectric constant $\mathbf{K}$ is a tensor quantity. Here $\mathbf{P}$ is the polarisation vector due to the displacement of electrons by the electric field of the wave as modified by the presence of the earth's magnetic field. If $\mathbf{S}$ denotes the displacement of the electron under these conditions, we have

$$\mathbf{P} = 4\pi N e \mathbf{S} \quad \dots \quad (1.2)$$

The displacement $\mathbf{S}$ is given by the Lorentz equation

$$\frac{d^2 \mathbf{S}}{dt^2} + \nu \frac{d \mathbf{S}}{dt} + \frac{e}{mc} \left[\mathbf{H} \times \frac{d \mathbf{S}}{dt} \right] = \frac{e}{m} \cdot \mathbf{E} \quad \dots \quad (1.3)$$

Replacing $\mathbf{S}$ by $\mathbf{P}$ and since $\mathbf{E}, \mathbf{S} \propto e^{i\omega t}$ we can easily find out the solution of (1.3) in the form

$$\mathbf{P} = A \cdot \Delta \mathbf{E}, \quad (1.2a)$$

where $A = r/\beta(\beta^2 - \omega^2)$ and Δ is a tensor quantity given by the matrix

$$\Delta = \begin{pmatrix} \omega_x^2 - \beta^2 & \omega_y \omega_x + i\beta \omega_z & \omega_z \omega_x - i\beta \omega_y \\ \omega_x \omega_y - i\beta \omega_z & \omega_y^2 - \beta^2 & \omega_z \omega_y + i\beta \omega_x \\ \omega_x \omega_z + i\beta \omega_y & \omega_y \omega_z - i\beta \omega_x & \omega_z^2 - \beta^2 \end{pmatrix} \quad (1.4)$$

Here $\beta = 1 - i\nu/p$ where ν = collision-frequency, $r = p_0^2/p^2$ where $p_0^2 = 4\pi N e^2/m$, N being the number of particles per c.c., $\omega = \mathbf{p}_h/p$ where $\mathbf{p}_h$ = circular gyromagnetic frequency = $e\mathbf{H}/mc$, $\omega_x, \omega_y, \omega_z$ are components of ω .

From (1.1), (1.2) and (1.4) we can write the complex dielectric tensor in the form

$$\mathbf{K} = \begin{pmatrix} 1 - A(\beta^2 - \omega_x^2) & A(\omega_x \omega_y + i\beta \omega_z) & A(\omega_x \omega_z - i\beta \omega_y) \\ A(\omega_x \omega_y - i\beta \omega_z) & 1 - A(\beta^2 - \omega_y^2) & A(\omega_z \omega_y + i\beta \omega_x) \\ A(\omega_x \omega_z + i\beta \omega_y) & A(\omega_x \omega_y - i\beta \omega_z) & 1 - A(\beta^2 - \omega_z^2) \end{pmatrix} \quad (1.4a)$$

So far the treatment has been quite general. Let us now consider the propagation of a plane wave along the vertical directions (axis of z) and the axis of y is chosen to be perpendicular to the magnetic meridian. Then putting $\omega_y=0$, $\mathbf{K}$ comes out as

$$\mathbf{K} = \begin{pmatrix} 1 - A(\beta^2 - \omega_x^2) & Ai\beta\omega_x & A\omega_x\omega_x \\ -Ai\beta\omega_x & 1 - A\beta^2 & Ai\beta\omega_x \\ A\omega_x\omega_x & -Ai\beta\omega_x & 1 - A(\beta^2 - \omega_x^2) \end{pmatrix} \quad (1.4b)$$

Introducing the condition $\nabla \cdot \mathbf{D} = 0$, i.e. $E_x + P_x = 0$ we get from (1.4b)

$$E_x = \frac{r\omega_x}{C'} (-\omega_x E_x + i\beta E_y) \quad (1.5)$$

$$\text{where } C' = \beta(\beta^2 - \omega^2) - r(\beta^2 - \omega^2)$$

Taking the curl of both sides of the second equation in (1.1) and putting $\frac{\partial}{\partial t} = i\beta$ we get the wave equation for the electric vector in the form

$$\nabla \times \nabla \times \mathbf{E} - \frac{\beta^2}{c^2} \mathbf{D} = 0 \quad (1.6)$$

Breaking up this equation into components and putting

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial y} = 0 \text{ we get } \frac{d^2 E_x}{dz^2} + \frac{\beta^2}{c^2} D_x = 0, \frac{d^2 E_y}{dz^2} + \frac{\beta^2}{c^2} D_y = 0 \quad (1.7)$$

From (1.6) and (1.7) we get after some simplification the following expressions for the Maxwell Displacement Vector

$$\begin{aligned} D_x &= K_1 E_x - iLE_y, & D_y &= K_2 E_y - iLE_x \\ K_1 &= 1 - r \frac{\beta^2 - r\beta - \omega_x^2}{C'}, & K_2 &= 1 - \frac{r(\beta^2 - r\beta)}{C'} \\ L &= r(r - \beta)\omega_x / C' \end{aligned} \quad (1.8)$$

Introducing the symbol $u = zp/c$, we get the equations of propagation of the electric vector as

$$\frac{d^2 E_x}{du^2} + K_1 E_x - iLE_y = 0; \quad \frac{d^2 E_y}{du^2} + K_2 E_y + iLE_x = 0 \quad (1.9)$$

Equations in these forms do not help us much in the understanding of the phenomenon unless the coupling term L vanishes, or $K_1 = K_2$. We have $L = 0$ when $\omega_x = 0$, i.e. at the magnetic equator (quasi-transverse case).

$K_1 = K_2$ when $\omega_x = 0$; this holds only for the magnetic poles (quasi-longitudinal case). These special cases are given in equations (1.17), (1.16).

For any latitude we try the following procedure. Multiply both sides of the second equation in (1.9) by some indeterminate quantity $i\rho$ and add the product to the first equation. Re-arranging the terms we get

$$\begin{aligned} \frac{d^2}{du^2} (E_x + i\rho E_y) + (K_1 - \rho L) E_x + (K_2 - L/\rho) i\rho E_y - 2i \\ \frac{d\rho}{du} \frac{dE_y}{du} - i \frac{d^2 \rho}{du^2} E_y = 0 \end{aligned} \quad (1.10)$$

Since we are free to choose ρ , it is advantageous to do it in such a way that the coefficients of E_x and $i\rho E_y$ are equal, i.e. we put

$$K_1 - \rho L = K_2 - L/\rho = q^2 \quad (1.11)$$

ρ is therefore given by the roots of the equation

$$\rho^2 - (K_1 - K_2)\rho/L - 1 = 0 \quad (1.12)$$

Now introducing the symbol

$$G = (K_1 - K_2)/2L = \frac{\omega_x^2}{2\omega_x(r - \beta)} \quad (1.13)$$

the two roots of equation (1.11), which can be denoted by ρ_1 and ρ_2 , can be written as:

$$\rho_1 = G - \sqrt{1 + G^2}; \quad \rho_2 = G + \sqrt{1 + G^2} \quad (1.14)$$

Now it can be easily shown that

$$C' = (\beta - r)(\beta + \rho_1\omega_x)(\beta + \rho_2\omega_x).$$

With the aid of this relation, it is easy to prove from (1.11) that q^2 has two values q_1^2 and q_2^2 given by

$$q_1^2 = 1 - \frac{r}{\beta + \rho_1\omega_x}, \quad q_2^2 = 1 - \frac{r}{\beta + \rho_2\omega_x} \quad (1.14a)$$

It is easy to see that these expressions are equivalent to Appleton expressions (for complex refractive index)². (Vide the expression given by him in the Report on the Progress of Physics, Vol. 2, 1936.)

We may now turn to the equations (1.10). If $d\rho/du$ and $d^2\rho/du^2$ can be neglected, we have the following equations of propagation for the two waves

$$\left. \begin{aligned} \text{O-wave: } \frac{d^2}{du^2} (E_x + i\rho_1 E_y) + q_1^2 (E_x + i\rho_1 E_y) &= 0 \\ \text{X-wave: } \frac{d^2}{du^2} (E_x + i\rho_2 E_y) + q_2^2 (E_x + i\rho_2 E_y) &= 0 \end{aligned} \right\} \quad (1.15)$$

The terms we have neglected are

$$-2i \frac{d\rho}{du} \frac{dE_y}{du} - i \frac{d^2 \rho}{du^2} E_y$$

Now we have

$$\frac{d\rho}{du} = \frac{d}{du} (G \mp \sqrt{1 + G^2}) \simeq \frac{dr}{dz} \simeq \frac{dV}{dz}$$

and can be neglected only when $\frac{dN}{dz} = 0$ or small. Equations (1.15) therefore hold when we can neglect dN/dz and d^2V/dz^2 , i.e. for a medium for which N varies very slowly.

The equations (1.15) take simplified forms at the geomagnetic equator and the poles. For the GM-equator we have, since $G = \infty$,

$$\rho_1 = G - \sqrt{1 + G^2} = 0, \quad \omega_x \rho_2 = 2G\omega_x = \frac{\omega_x^2}{r - \beta}$$

Hence we have

$$q^2 = 1 - \frac{\tau}{\beta}, \quad q_1 = 1 - \frac{\tau}{\beta - \frac{\omega^2}{\beta - \tau}}$$

and the equations (1.15) have the form

$$\left. \begin{aligned} \text{(O-wave): } & \frac{d^2 E_x}{du^2} + \left(1 - \frac{\tau}{\beta}\right) E_x = 0 \\ \text{(X-wave): } & \frac{d^2 E_x}{du^2} + \left(1 - \frac{\tau}{\beta - \frac{\omega^2}{\beta - \tau}}\right) E_x = 0 \end{aligned} \right\} \quad (1.16)$$

For the poles, we have $G=0$, $\rho_2=1$, $\rho_1=-1$, and $\omega_2=-\omega$ at the north pole, and $=\omega$ at the south pole. Hence we have the equations

$$\left. \begin{aligned} \text{(O-wave): } & \frac{d^2}{du^2} (E_x - iE_y) + \left(1 - \frac{\tau}{\beta \pm \omega}\right) (E_x - iE_y) = 0 \\ \text{(X-wave): } & \frac{d^2}{du^2} (E_x + iE_y) + \left(1 - \frac{\tau}{\beta \mp \omega}\right) (E_x + iE_y) = 0 \end{aligned} \right\} \quad (1.17)$$

The upper sign refers to the N-magnetic pole, the lower to the S-magnetic pole.

More rigorous equations of propagation can be deduced by rotating the axes through a complex angle ϕ . We start from (1.9) and put

$$\begin{pmatrix} E_x \\ iE_y \end{pmatrix} = \begin{pmatrix} \cos \phi & -\sin \phi \\ \sin \phi & \cos \phi \end{pmatrix} \begin{pmatrix} V \\ W \end{pmatrix} = S \begin{pmatrix} V \\ W \end{pmatrix}$$

where S denotes the matrix given above. The inverse matrix

$$S^{-1} = \begin{pmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{pmatrix} \text{ and we have } \begin{pmatrix} V \\ W \end{pmatrix} = S^{-1} \begin{pmatrix} E_x \\ iE_y \end{pmatrix}$$

Then it can be easily shown that if by $\dot{E}_x$ we denote $\frac{dE_x}{du}$, etc.

$$\begin{pmatrix} E_x \\ iE_y \end{pmatrix} = S \begin{pmatrix} V \\ W \end{pmatrix}, \quad \begin{pmatrix} \dot{E}_x \\ i\dot{E}_y \end{pmatrix} = S \begin{pmatrix} V' \\ W' \end{pmatrix}$$

where

$$\dot{V} = \frac{dV}{du}, \quad \ddot{V} = \frac{d^2 V}{du^2}, \text{ etc.};$$

$$V' = \dot{V} - \dot{\phi} W, \quad W' = \dot{W} + \dot{\phi} V;$$

$$V'' = \frac{dV'}{du} - \dot{\phi} W' = \ddot{V} - 2\dot{\phi} \dot{W} - \ddot{\phi} W - \dot{\phi}^2 V;$$

$$W'' = \frac{dW'}{du} + \dot{\phi} V' = \ddot{W} + 2\dot{\phi} \dot{V} + \ddot{\phi} V - \dot{\phi}^2 W.$$

It is easy to see that V' , W' are the moving co-ordinate derivatives of V and W . Hence the fundamental equations (1.9) can be written as

$$(V'' - K_1 V - L W) \cos \phi - (W'' + K_1 W - L V) \sin \phi = 0, \quad (1.18)$$

$$(V'' - K_2 V - L W) \sin \phi - (W'' + K_2 W - L V) \cos \phi = 0.$$

From these equations, it is easy to deduce the following equations:

$$\begin{aligned} V'' + \{K_1 \cos^2 \phi + K_2 \sin^2 \phi - 2L \sin \phi \cos \phi\} V \\ - \{(K_1 - K_2) \sin \phi \cos \phi + L(\cos^2 \phi - \sin^2 \phi)\} W = 0 \end{aligned} \quad (1.19a)$$

$$\begin{aligned} W'' + \{K_1 \sin^2 \phi + K_2 \cos^2 \phi + 2L \sin \phi \cos \phi\} W \\ - \{(K_1 - K_2) \sin \phi \cos \phi + L(\cos^2 \phi - \sin^2 \phi)\} V = 0 \end{aligned} \quad (1.19b)$$

We observe that the coefficient of cross-terms, i.e. of W in (1.19a) and of V in (1.19b) have the same value. This may be made to vanish by appropriate choice of ϕ ,

$$\text{i.e. putting } (K_1 - K_2)/2L = G = -\cot 2\phi \quad (1.20)$$

If we put $\tan \phi = \tau$, the above equation is equivalent to $\tau^2 - 2\tau G - 1 = 0$, or $\tau = \tan \phi = G \pm \sqrt{1 + G^2} = \rho_1, \rho_2$.

As before, we denote by ρ_1 the quantity $G + \sqrt{1 + G^2}$. Then the other value of

$$\tau = -\frac{1}{\rho_1} = \rho_2 = G - \sqrt{1 + G^2}.$$

It can be easily shown that the coefficients of V and W in (1.19a) and (1.19b) viz.,

$$K_1 \cos^2 \phi + K_2 \sin^2 \phi - 2L \sin \phi \cos \phi = q^2$$

$$K_1 \sin^2 \phi + K_2 \cos^2 \phi + 2L \sin \phi \cos \phi = q^2$$

We have therefore the final equations:

$$V'' - q^2 V = 0; \quad W'' - q^2 W = 0$$

Now

$$V = E_x \cos \phi + iE_y \sin \phi = \frac{E_x + \omega_1 E_y}{\sqrt{1 + \rho_1^2}}$$

$$W = -E_x \sin \phi + iE_y \cos \phi = \frac{E_x - i\rho_2 E_y}{\sqrt{1 - \rho_2^2}} \quad (1.21)$$

Hence the equations written in full are:—

$$\left. \begin{aligned} \text{(O-wave)} \quad & \frac{d^2 V}{du^2} + (q^2 - \dot{\phi}^2) V = 2\dot{\phi} \dot{W} - \ddot{\phi} W \\ \text{(X-wave)} \quad & \frac{d^2 W}{du^2} - (q^2 - \dot{\phi}^2) W = -2\dot{\phi} \dot{V} - \ddot{\phi} V \end{aligned} \right\} \quad (1.22)$$

If the coupling term $\dot{\phi} = \frac{d}{du} \tan^{-1} \rho = \frac{d\rho/du}{1 - \rho^2}$ can be put

equal to zero, then equations (1.22) reduce to the equations (1.15). The coupling term is discussed in detail in the next section.

The advisability of rotating the axes through an angle ϕ is easily suggested from analogy of the present case to that of crystal optics. We write the equation (1.7) in the form

$$\frac{d^2 \mathbf{E}}{du^2} - \mathbf{D} = 0$$

¹ This type of equations was given by Rydbeck in 1950, but the signs of the right hand side of the equations were given as same. This is clearly a mistake, the signs ought to be opposite.

where the vector $\mathbf{E}$ has E_x and iE_y as the components and the vector $\mathbf{D}$ is given by

$$\begin{pmatrix} D_x \\ iD_y \end{pmatrix} = \begin{pmatrix} K_1 & -L \\ -L & K_2 \end{pmatrix} \begin{pmatrix} E_x \\ iE_y \end{pmatrix}$$

Since the tensor connecting $\mathbf{D}$ and $\mathbf{E}$ is a symmetrical tensor we write the equation of the tensor-ellipsoid as

$$\mathbf{D} \cdot \mathbf{E} = K_1 E_x^2 - 2LE_x \cdot iE_y + K_2 (iE_y)^2$$

from which we find out the principal axes, by the customary method of removing the cross term. We put

$$E_x = V \cos \phi - W \sin \phi, \quad iE_y = V \sin \phi + W \cos \phi.$$

This is equivalent to our transformation. The rest is identical.

The tensor-ellipsoid now takes the form

$$\mathbf{D} \cdot \mathbf{E} = q^2 V^2 + q^2 W^2 = f.$$

ϕ is the angle between the major axis of the ellipse and the magnetic meridian.

If $\frac{dN}{dz} = 0$ it retains a constant value. (See discussion in the next section.) We observe from (1.22) that the two modes of propagation are characterised by the phase velocities c/q_o , c/q_e and their respective polarisations are given by $i\rho_1$ and $i\rho_2$ (*vide infra*.)

It is not easy to deduce simple equations for the magnetic vectors. They are of the fourth degree. But some simplified relations can be deduced from the fundamental Maxwell equations. From the relation (1.1) we have

$$\frac{dH_x}{du} = -LE_x + iK_2 E_y, \quad i \frac{dH_y}{du} = K_1 E_x - L \cdot iE_y$$

or expressing E_x and iE_y in terms of V and W , we have

$$\begin{pmatrix} \dot{H}_x \\ i\dot{H}_y \end{pmatrix} = \begin{pmatrix} K_2 \sin \phi - L \cos \phi & K_2 \cos \phi + L \sin \phi \\ K_1 \cos \phi - L \sin \phi & -K_1 \sin \phi - L \cos \phi \end{pmatrix} \begin{pmatrix} V \\ W \end{pmatrix}$$

or

$$\left. \begin{aligned} V &= (\dot{H}_x \sin \phi + i\dot{H}_y \cos \phi) / q^2 = E_x \cos \phi + iE_y \sin \phi \\ W &= (\dot{H}_x \cos \phi + i\dot{H}_y \sin \phi) / q^2 = -E_x \sin \phi + iE_y \cos \phi \end{aligned} \right\} \quad (1.23)$$

From these expressions, which are exact, it is not possible to deduce any simple relation between the magnetic and electric vectors at any point. Only at the ground ($r=0$) where

$$q^2 = q_e^2 = 1, \text{ we have } E_x = i\dot{H}_y, \quad iE_y = \dot{H}_x \quad (1.24)$$

but these relations are not applicable for any other point.

§2. POLARISATION AND COUPLING.

Expressions (1.22) represent the most rigorous equations for vertical propagation of e.m. waves in the ionosphere. The electric vectors E_x , E_y are coupled by the quantities

ρ_1 and ρ_2 forming two new vectors V and W given by (1.21) and equations for V and W are coupled by the factor ϕ . As shown earlier V may be identified with the electric vector for the o -mode of propagation, with the corresponding quantity W for the e -mode.

The general form of solution of (1.22) can be written in the forms:

$$\left. \begin{aligned} V &= (E_x + i\rho_1 E_y) / \sqrt{1 + \rho_1^2} \simeq e^{i\rho_1 t} \cdot f_V(z) \\ \text{and } W &= (E_x + i\rho_2 E_y) / \sqrt{1 + \rho_2^2} \simeq e^{i\rho_2 t} \cdot f_W(z) \end{aligned} \right\} \quad (2.1)$$

or since ρ_1 and ρ_2 are both functions of z , we can write:

$$E_x + i\rho_1 E_y \simeq e^{i\rho_1 t} \cdot \psi_V(z), \quad E_x + i\rho_2 E_y \simeq e^{i\rho_2 t} \cdot \psi_W(z)$$

where both ψ_V and ψ_W are complex functions of the real variable z .

Let us now put

$$i\rho_1 = R e^{i\alpha} \text{ and consequently } i\rho_2 = R^{-1} e^{-i\alpha} \quad (2.1a)$$

Therefore we have

$$\left. \begin{aligned} E_x \cdot e^{-i\rho_1 t} + R E_y \cdot e^{-i(\rho_1 t - \alpha)} &= \psi_1(z) \\ E_x \cos \rho_1 t + R E_y \cos (\rho_1 t - \alpha) &= \text{Re} |\psi_1(z)| = A_V \\ E_x \sin \rho_1 t + R E_y \sin (\rho_1 t - \alpha) &= \text{Im} |\psi_1(z)| = B_V \end{aligned} \right\} \quad (2.2)$$

where A and B are functions of z .

Hence we have for the V -wave:

$$E_x^V = \frac{C_V}{\sin \alpha} \sin (\rho_1 t - \alpha + \pi - \theta_V), \quad E_y^V = \frac{C_V}{R \sin \alpha} \sin (\rho_1 t - \theta_V) \quad (2.3)$$

where $C_V = \sqrt{A_V^2 + B_V^2}$, $\theta_V = \tan^{-1} (B_V / A_V)$.

Similarly for the W -wave, we get

$$E_x^W = \frac{RC_W}{\sin \alpha} \sin (\rho_2 t - \alpha - \theta_W), \quad E_y^W = \frac{C_W}{\sin \alpha} \sin (\rho_2 t + \pi - \theta_W)$$

where

$$C_W = \sqrt{A_W^2 + B_W^2}, \quad \theta_W = \tan^{-1} (B_W / A_W) \quad (2.4)$$

The phase-angle α and the amplitude ratio R are in general functions of δ , ω , r and θ , and we discuss presently how to obtain analytical expressions for R and α .

Magnetic Damping Factor: We denote the magnetic condition of the locality by the angle of propagation θ , which is the angle between the upward vertical direction and the positive direction of the magnetic lines of force. Therefore

$$\omega_z = -|\omega| \cos \theta, \quad \omega_x = -|\omega| \sin \theta \quad (2.5)$$

because $\omega = \frac{e\mathbf{H}}{mc\beta}$, and $e = -|e|$ for electrons;

$$\text{put } \nu_e = \rho \omega_x^2 / 2\omega_z = -\frac{|p_h|}{2 \cos \theta} \cdot \sin^2 \theta. \quad (2.6)$$

ν_e is positive in the N.H. and negative in S.H. $|\nu_e|$ varies from 0 at the poles to ∞ at the equator, and its value for a

number of stations in the N.H. is shown in row 6 of Table III. Let us denote ν_c/p by δ_c which may be termed the magnetic damping ratio. Then introducing the quantities ξ and η defined by

$$\xi = \frac{\delta}{\delta_c}, \quad \eta = \frac{1-r}{\delta_c}, \quad \tan \gamma = \frac{\delta}{1-r} \quad (2.7)$$

$$\text{we have } G = \frac{\delta_c}{r-\beta} = \frac{1}{-\eta+i\xi} = -\left(\frac{\eta}{\eta^2+\xi^2} + i\frac{\xi}{\eta^2+\xi^2}\right) \quad (2.8)$$

We shall now show that it is convenient to represent R, α and other quantities on a ξ, η -plane. Let us first discuss the possible range of values of ξ and η .

THE ξ, η -PLANE

We have $\xi = \nu/\nu_c$; hence ξ is positive in the N.H., and negative in the S.H. $|\xi|$ varies from ∞ at the poles to 0 at the G.M.E. Large values of ξ denote large damping, small values small damping. $\xi=0$ indicates no damping.

As $|\delta_c|$ varies from 0 at the pole to ∞ at the G.M.E., the particular values of ξ which refer to E or F -regions at any locality will have to be found for every locality separately.

Let us now trace the values $\eta = \frac{1-r}{\delta_c}$. In the N.H., since δ_c is positive, we have on the ground $r=0$, $\eta=1/\delta_c$. This is the maximum value of η below $r=1$. As we take higher points in the ionosphere, $r = \frac{4\pi N_c^2}{m\beta^3}$ becomes appreciable, the value of η decreases and it becomes zero at $r=1$, after which for $r>1$, η is negative. Therefore the line $r=1$, which corresponds to $\eta=0$, divides the $\xi\eta$ -plane in two parts.

Let us now try to find out general analytical expressions for R and α at any height, i.e. for any value of r and δ , as functions of ξ and η . We proceed from the expressions

$$\left. \begin{aligned} Re^{i\alpha} &= i\rho_1 = iG\{1 - \sqrt{1+1/G^2}\} \\ R^{-1}e^{-i\alpha} &= i\rho_2 = iG\{1 + \sqrt{1+1/G^2}\} \end{aligned} \right\} \quad (2.9)$$

Now using (2.6) and (2.7), we have

$$(R+R^{-1}) \cos \alpha + i(R-R^{-1}) \sin \alpha = 2iG$$

from which we deduce the two relations

$$(R+R^{-1}) \cos \alpha = \frac{2\xi}{\eta^2+\xi^2}, \quad (R-R^{-1}) \sin \alpha = -\frac{2\eta}{\eta^2+\xi^2} \quad (2.10)$$

From (2.9), we deduce the important relation

$$\cos 2\alpha = \frac{1}{\lambda^2} - \sqrt{1 + \frac{2}{\lambda^2} \cos 2\gamma + \frac{1}{\lambda^4}} \quad (2.11)$$

where $\lambda^2 = \xi^2 + \eta^2$

The sign before the radical is ± 1 . We have retained only the negative sign after comparison with the limiting

case of a friction-free atmosphere. The following expressions for R can be easily verified

$$\left. \begin{aligned} R^2 &= \frac{\xi \tan \alpha - \eta}{\xi \tan \alpha + \eta} \\ R &= \frac{1}{\lambda^2} \left\{ \frac{\xi}{\cos \alpha} - \frac{\eta}{\sin \alpha} \right\} \\ R^{-1} &= \frac{1}{\lambda^2} \left\{ \frac{\xi}{\cos \alpha} + \frac{\eta}{\sin \alpha} \right\} \end{aligned} \right\} \quad (2.12)$$

There are some inherent ambiguities in these expressions for R and α which must be removed. This can be done if we follow the course of the complex quantities ρ_1 and ρ_2 in the complex plane and always confine ourselves to one particular branch in discussing the nature of ρ_1, ρ_2 .

For this purpose we start with expressions (2.9).

Now

$$1 + \frac{1}{G^2} = \{1 - \xi^2 + \eta^2\} - 2i\xi\eta \quad (2.13)$$

when $r=0$, $Im \left\{1 + \frac{1}{G^2}\right\} = -2\xi\eta$ and it is definitely negative. Hence, if we plot $1 + \frac{1}{G^2}$ in the complex plane, the point representing it must be in the third or the fourth quadrant. Therefore, the point $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ which is double-valued, must have one of its values in the fourth quadrant, and therefore, the other will be in the second quadrant.

We now choose $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ to be given by the point in the fourth quadrant for $r=0$.

Now let r increase; when $r=1$, $Im \left\{1 + \frac{1}{G^2}\right\} = 0$ and as (2.11) shows

$$Re \left\{1 + \frac{1}{G^2}\right\} > 0 \text{ if } \xi < 1, \text{ and } < 0 \text{ if } \xi > 1.$$

Hence, at $r=0$, and for $\xi < 1$, $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ is either real positive or real negative. But the last alternative is ruled out as we have $\left\{1 + \frac{1}{G^2}\right\}^{\frac{1}{2}}$ in the fourth quadrant. Hence $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ is real positive for $r=1$, $\xi < 1$. Similarly for $\xi < 1$, $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ is negative imaginary. For $r > 1$, and $\xi < 1$, $Im \left\{1 + \frac{1}{G^2}\right\}$ is > 0 , and $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ is in the first quadrant, while for $\xi > 1$, $\left(1 + \frac{1}{G^2}\right)^{\frac{1}{2}}$ is in the third quadrant, i.e., the real part is negative.

Thus $Re \left\{ 1 + \frac{1}{G^2} \right\}^{\frac{1}{2}}$ is always positive except when $\xi > 1$ and $r > 1$. In this case $Re \left\{ 1 + \frac{1}{G^2} \right\}^{\frac{1}{2}}$ is negative.

Now from (2.9), we have

$$\frac{|\rho_1|}{|\rho_2|} = R^2 = \left(\frac{1 - 2A \cos \beta + A^2}{1 + 2A \cos \beta + A^2} \right)^{\frac{1}{2}}$$

where $A \cos \beta = Re \left\{ 1 + \frac{1}{G^2} \right\}^{\frac{1}{2}}$

Hence, in general $R^2 \leq 1$, except for the quadrant $\xi > 1$, $r > 1$, in which case, since $Re \left\{ 1 + \frac{1}{G^2} \right\}^{\frac{1}{2}} < 0$, $R^2 > 1$.

Putting $\tan \gamma = t$, we have from (2.10)

$$\cos \alpha = \frac{1}{\xi} \cdot \frac{2t^2}{1+t^2} \cdot \frac{R}{R^2+1}$$

$$\sin \alpha = \frac{1}{\xi} \cdot \frac{2t}{1+t^2} \cdot \frac{R}{1-R^2}$$

Let us take N.H. Since ξ is positive, we have $\cos \alpha > 0$ and $\sin \alpha > 0$ for $r < 1$; and for $r > 1$ and $\eta < 1$, $\sin \alpha$ is negative; for $r > 1$ and $\xi > 1$, $\sin \alpha > 0$.

For ready reference we have given in Table I the signs and ranges of R and α for the different regions in the $\xi\eta$ -plane.

Before taking the general case, let us consider how R and α vary along the central line $\eta = 0$. We have now $G = -i/\xi$, hence, we have

$$Re^{i\alpha} = \frac{1}{\xi} \left\{ 1 - \sqrt{1 - \xi^2} \right\}$$

Now if $\xi < 1$, $\alpha = 0$, $R = \frac{1}{\xi} - \left(\frac{1}{\xi^2} - 1 \right)^{\frac{1}{2}}$ } (2.14)

but if $\xi > 1$, $Re^{i\alpha} = \frac{1}{\xi} \left\{ 1 \pm i \left(1 - \frac{1}{\xi^2} \right)^{\frac{1}{2}} \right\}$ }

Hence $R \cos \alpha = 1/\xi$, $R \sin \alpha = \pm (1 - 1/\xi^2)^{\frac{1}{2}}$
 $R = 1$, $\cos \alpha = 1/\xi$.

This shows that the line $\xi = 1$, divides the $\xi\eta$ -plane in two regions. On the left-hand side, we have $\alpha = 0$ all along the abscissa, up to $\xi = 1$; on the right-hand side $\alpha = \cos^{-1} 1/\xi$ and, therefore, varies from 0 at $\xi = 1$ to $\pi/2$ at $\xi = \infty$. The value of R on the abscissa is $= 1$, if $\xi > 1$ but for $\xi < 1$ it is given by (2.14).

THE $\alpha = \text{CONST.}$ CURVES:

For the N.H. ξ is always positive. The lines $\xi = 1$, and $\eta = 0$ (figs. 1 and 2) divide the plane into four sections (I, II, III, IV) as shown above. We can find out the value of α with the aid of (2.11), and for its sign, we have to look to Table II. (2.11) can also be written as:

$$\frac{(\xi/\lambda^2)^2}{\cos^2 \alpha} - \frac{(\eta/\lambda^2)^2}{\sin^2 \alpha} = 1 \quad (2.15)$$

$$\text{or} \quad \frac{\lambda^2}{2} \sin^2 2\alpha + \cos 2\gamma + \cos 2\alpha = 0 \quad (2.15a)$$

When we wish to draw curve $\alpha = \text{const.}$, we can do so by using (2.11 or 2.15a). A few curves are given in fig. (1, 2). It is seen that for $\alpha > 0$, these curves all cut the abscissa at right angles at $\xi = \sec \alpha$. The point (0, 0), through which the curve appears to pass is to be excluded,

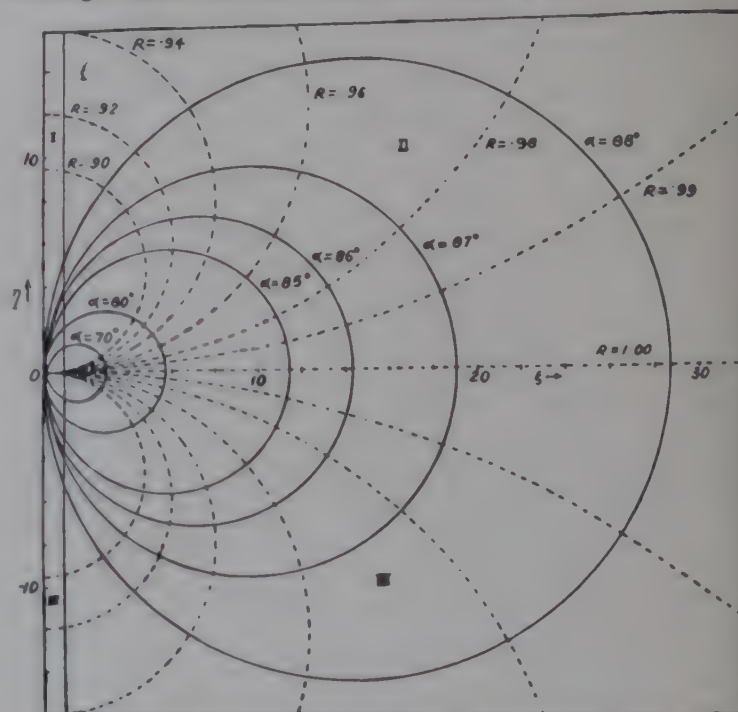


Fig. 1

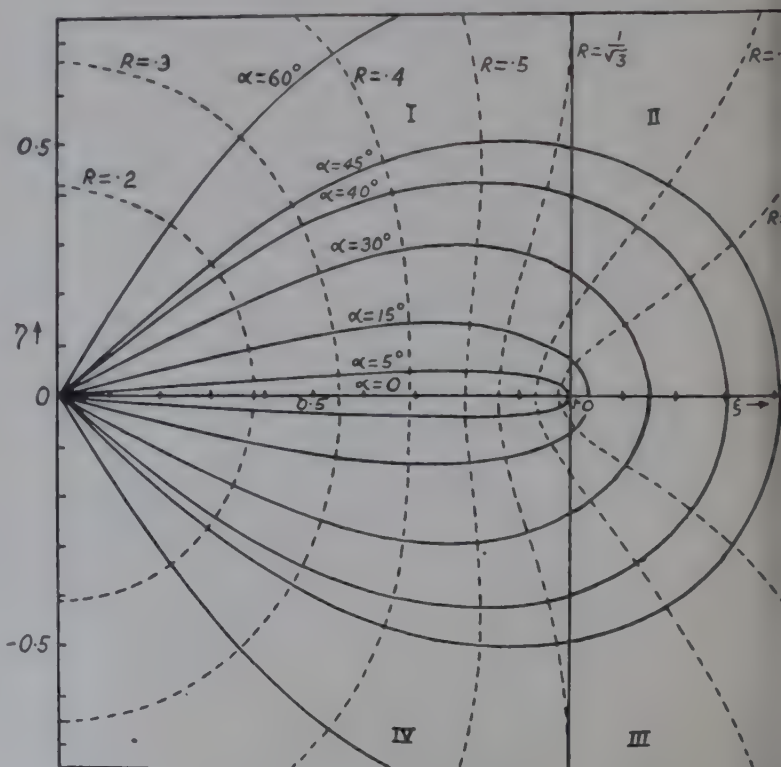


Fig. 2

but the curves approach this point at the angle $\pi/2 - \gamma$ to the abscissa.

The sign of α is positive in sections I, II, III, but is negative in section IV. We have $\alpha=0$ for the abscissa up to $\xi=1$; on the ordinate $\alpha=\pi/2$ above the abscissa and $=-\pi/2$ below.

Let us see how to draw the curves $R=\text{const.}$ It can be shown from (2.12) that

$$\left(\frac{\xi}{\lambda^2}\right)^2 \left| \left(\frac{2R}{1+R^2}\right)^2 + \left(\frac{\eta}{\lambda^2}\right)^2 \right| \left(\frac{2R}{1-R^2}\right)^2 = 1. \quad (2.16)$$

Now let us put $R=\tan\psi$; then $\sin 2\psi = \frac{2R}{1+R^2}$, $\tan 2\psi = \frac{2R}{1-R^2}$; we can rewrite in the form

$$\lambda^2 = \sin^2 2\psi \{1 + \tan^2 2\psi \cos^2 \gamma\} \quad (2.16a)$$

This gives us the polar equation in the $\xi\eta$ -plane for $R=\text{const.}$ curves; when $R < 1$ we have $\sin 2\psi = 2R < 1$ and (2.16a) reduces to $\lambda^2 = (2R)^2$, i.e., the $R=\text{const.}$ curves are circles. But as R becomes larger, we have curves as shown in figs. (1, 2). We observe that for $R < 1$, these curves cut the abscissa ($\gamma=\pi/2$) at $\xi = \sin 2\psi = \frac{2R}{1+R^2}$, and the ordinate ($\gamma=0$) at $\eta = \tan 2\psi = \frac{2R}{1-R^2}$. The curves crowd as we approach the point $\xi=1$.

So far the $R=\text{const.}$ curves are confined to sections I and IV. Let us now take sections II and III. From the expression

$$R^2 = (\xi \tan \alpha - \eta) / (\xi \tan \alpha + \eta)$$

We have $R \leq 1$ in section II, but in Section III we have

$$R^2 = \frac{\xi \tan \alpha + |\eta|}{\xi \tan \alpha - |\eta|} > 1$$

i.e., at the mirror points (ξ, η) , $(\xi, -\eta)$, the values of R are reciprocal to each other. In Section II, $R < 1$, and in section III, $R > 1$.

The $R=\text{constant}$ curves for graded values of R are shown in figs. (1 and 2). In I, II and IV, $R < 1$, while in III R should be read as $1/R$, so that $R > 1$ in this section.

It is to be noticed that for $R < \frac{1}{\sqrt{3}}$ the curves are confined

to the left-hand side of $\xi=1$. The curve $R = \frac{1}{\sqrt{3}}$ touches

the line $\xi=1$, and the curves with $R > \frac{1}{\sqrt{3}}$ cut $\xi=1$ at two points. For values of $R \approx 1$, the $R=\text{constant}$ curves

are nearly circles with centres at $(0, \pm \frac{R}{1-R^2})$ and radius

$\frac{R}{1-R^2}$ except very near the point $\xi=0, \eta=0$. The family of $R=\text{constant}$ curves cuts orthogonally the family of $\alpha=\text{constant}$ curves.

Scott (1950) has drawn curves similar to those given in figures (1 and 2).

Let us now study the polarisation of the incident and reflected waves in the light of the above discussion. The following table gives the phases for the general and some particular cases, of the eight field quantities E and H for both V and W -waves.

The figures in column 2 are obtained from (2.3), (2.4). For others see *infra*.

We have at present no means for determining θ_V and θ_W . For the ground, however, since $r=0, \delta=0$ and $\alpha=\pi/2$ for the N.H. we can easily write out the phase differences. They are given in column 3.

We have, therefore, for the ground

$$E_x^V = C_V \cos pt, \quad E_y^V = \frac{C_V}{R} \sin pt, \quad E_x^W = C_W \cos pt,$$

TABLE I

	Phase Angles	Phase Difference $r=0, \nu=0$	Phase Difference at $\eta=0$		Phase Difference	
			$ \xi > 1, \xi > 0$	$ \xi < 1, \xi > 0$	$ \xi > 1, \xi < 0$	$ \xi < 1, \xi < 0$
E_x^V	$\pi - \alpha - \theta_V$	$\pi/2$	$\pi - \sec^{-1} \xi $	π	$\sec^{-1} \xi $	0
E_y^V	$-\theta_V$	0	0	0	0	0
E_x^W	$\alpha - \theta_W$	$\pi/2$	$\sec^{-1} \xi $	0		π
E_y^W	$\pi - \theta_W$	π	π	π	$\pi + \sec^{-1} \xi $	π
H_x^V		0			π	
H_y^V		$-\pi/2$				
H_x^W		π				
H_y^W		$+\pi/2$				

$$E_v^W = -RC_W \sin pt,$$

$$H_z^V = \frac{C_V}{R} \sin pt, H_v^V = -C_V \cos pt, H_z^W = -RC_W \sin pt,$$

$$H_v^W = -C_W \cos pt.$$

The value of R can be obtained directly from (2.12) or from the condition $\eta = 2R/1(-R^2)$. We have generally for any point on $\xi = 0$ (no damping),

$$R = \sqrt{1 + 1/\eta^2} - \frac{1}{\eta}$$

and for $r=0$, we have

$$R = \sqrt{1 + \delta_c^2} - \delta_c.$$

The polarisation-ellipses described by E and H for V and W -waves and their senses of rotation are shown in the figures given below for an assumed value of $R = -6$.

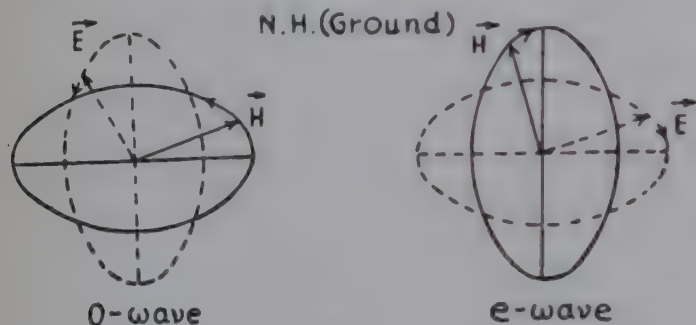


Fig. 3

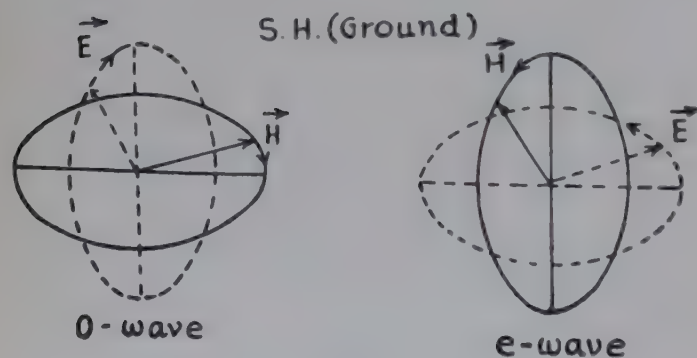


Fig. 4

It is instructive to see how the polarisation varies with height. For $r=1$ we can easily deduce the values of the relative phase angles for E with the aid of the above relations which are given in columns 4 and 5 of Table I. We have not given phase-angles for H , as relation (1.24) then no longer holds. We have now for $\xi = \infty$, $r=1$.

$$E_z^V = C_V \cos pt, E_v^V = C_V \sin pt, E_z^W = C_W \cos pt, \\ E_v^W = -C_W \sin pt.$$

These are circles as shown in fig. 5(e).

For $\xi > 1$, $r=1$, putting $\alpha = \cos^{-1} \frac{1}{\xi}$

$$E_z^V = -\frac{C_V}{\sqrt{1-1/\xi^2}} \sin(pt-\alpha), \quad E_v^V = \frac{C_V}{\sqrt{1-1/\xi^2}} \sin pt;$$

$$E_z^W = \frac{C_W}{\sqrt{1-1/\xi^2}} \sin(pt+\alpha), \quad E_v^W = -\frac{C_W}{\sqrt{1-1/\xi^2}} \sin pt.$$

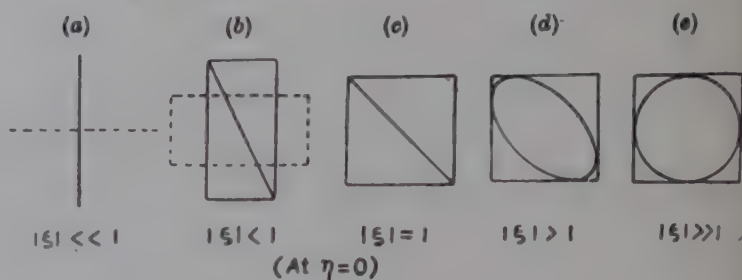


Fig. 5

These are ellipses, circumscribed within a square as shown in fig. 5(a), the contact points being given by (2.17a) and the ratio of axes are $\sqrt{(\xi-1)/(\xi+1)}$, the angle of tilt being $\pi/4$. For $\xi=1$, $r=1$,

$$E_z^V \simeq -\sin pt, E_v^V \simeq \sin pt, E_z^W \simeq \sin pt, E_v^W \simeq -\sin pt$$

The ellipse reduces to a straight line coincident with the diagonal of the square. For $\xi < 1$, $r=1$.

$$E_z^V = -\sin pt, E_v^V = R^{-1} \sin pt, E_z^W \simeq \sin pt, E_v^W = R \sin pt$$

This is shown in fig. 5(c).

For $\xi > 1$, the curves are lines forming diagonals of two oblongs as shown in fig. 5(b), the ratio of the sides of the oblongs being given by R or R^{-1} .

When $\xi=0$, $r=1$, we have $R=0$, $R^{-1}=\infty$ and the polarisation ellipses reduce to two straight lines parallel to the magnetic axis and perpendicular to it (Fig. 5(a).)

Figures of polarisation ellipses for $r=1$ have been given by Booker (1934) for the magnetic vector. It will be seen that the diagonal lines in our figures are in the first and third quadrants. This is because we have drawn polarisation ellipses for E , while Booker has drawn for H .

In general, omitting θ_V and θ_W we have for any point of the ionosphere where R and α have the values given in Table II

$$E_z^V = -\frac{C_V}{\sin \alpha} \sin(pt-\alpha), \quad E_v^V = \frac{C_V}{R \sin \alpha} \sin pt,$$

$$E_z^W = \frac{C_W}{\sin \alpha} \sin(pt+\alpha), \quad E_v^W = -\frac{RC_W}{\sin \alpha} \sin pt.$$

Now eliminating pt we deduce the following equations for the ellipses described by E_z and E_v :

$$\left. \begin{aligned} (E_z^V)^2 + 2R \cos \alpha \cdot E_z^V E_v^V + R^2 (E_v^V)^2 &= C_V^2 \\ (E_z^W)^2 + 2R^{-1} \cos \alpha \cdot E_z^W E_v^W + R^{-2} (E_v^W)^2 &= C_W^2 \end{aligned} \right\} \quad (2.17)$$

TABLE II

$\xi = \frac{\delta}{\delta c}$	$\eta = \frac{1-r}{\delta c}$	$ip = Re^{i\alpha}$		Polarisation of the electric vector	
		R	α	Nature of polarisation	Sense of rotation
$ \xi = 0, \delta = 0$	$\eta > 0$	$\frac{\sqrt{1+\eta^2}-1}{ \eta }$	$+\frac{\pi}{2}$	Ellipse; ratio of axes = R ; Tilt angle = 0 (o -wave and ϵ -wave)	Anticlockwise for o -wave and Clockwise for ϵ -wave
	$\eta < 0$	Do.	$-\frac{\pi}{2}$	Do.	Clockwise for o -wave and anti- clockwise for ϵ -wave
$ \xi < 1$	$\eta = 0, (r=1)$	$\frac{1-\sqrt{1-\xi^2}}{ \xi }$	0 for $\xi > 0$, π for $\xi < 0$	Linear, tilt-angle $\tan^{-1}(-R)$ and $\tan^{-1}\left(\frac{1}{R}\right)$ for two waves	
$ \xi = 1$	$\eta = 0, (r=1)$	1	Do.	Linear, tilt-angle $-\pi/4$ and $+\pi/4$.	
$ \xi > 1$	$\eta = 0, (r=1)$	1	$\sec^{-1} \xi $, 1st Quadrant for $\xi > 0$, 3rd for $\xi < 0$	Ellipse, ratio of axes = $\sqrt{\frac{ \xi -1}{ \xi +1}}$ Tilt-angle $-\pi/4$ and $+\pi/4$	Anticlockwise for o -wave and Clockwise for ϵ -wave
	$\eta > 0, \xi < 1$	$R \leq 1$	$0 \leq \alpha \leq \pi/2$	Ellipse, defined by eqn. (2.17)	Anticlockwise for o -wave and Clockwise for ϵ -wave
	$ \xi > 1$	$R \leq 1$	$0 \leq \alpha \leq \pi/2$	Do.	Do. Clockwise for o -wave and Anticlockwise for ϵ -wave
$\xi > 0, (N. H.)$	$ \xi < 1$	$R \leq 1$	$-\pi/2 \leq \alpha \leq 0$	Do.	Do.
	$\pi < 0$	$R \geq 1$	$0 \leq \alpha \leq \pi/2$	Do.	Do.
$\xi < 0, (S. H.)$	$ \xi < 1$	$R \leq 1$	$\pi/2 \leq \alpha \leq \pi$	Do.	Do.
	$\pi > 0, \xi > 1$	$R \geq 1$	$\pi \leq \alpha \leq 3\pi/2$	Do.	Do.
	$ \xi < 1$	$R \leq 1$	$\pi \leq \alpha \leq 3\pi/2$	Do.	Anticlockwise for o -wave and Clock- wise for ϵ -wave
	$\eta < 0, \xi > 1$	$R \leq 1$	$\pi \leq \alpha \leq 3\pi/2$	Do.	
$\xi = 0, \delta c = \infty, \delta \neq 0$ Equator)	$\eta > 0, (+\infty)$	0	$\tan^{-1}\frac{(1-r)}{\delta}$ $\rightarrow 0$ for N. H. and π for S. H. as $\gamma \rightarrow 1$	Linear polarisation, Tilt = 0	
	$\eta < 0, (-\infty)$	0	Do.	Linear polarisation, Tilt = 0	
$\xi = \infty, \delta c = 0, \delta \neq \infty$ (Pole)	$\eta < 0$	1	$+\pi/2$	Circular polarisation	Anticlockwise for o -wave and Clock- wise for ϵ -wave
	$\eta < 0$	1	$-\pi/2$	Do.	Clockwise for o -wave and Anticlockwise for ϵ -wave
Ground	(N. H.)	$\sqrt{1+\delta c^2}-1 \delta c$		Ellipses, given by equation (2.17)	Sense of rotation shown in figs. (3) and (4)
Ground	(S. H.)	Do.		Do.	Do.

The axes of the polarisation ellipses are tilted with respect to x -axis through the angle ψ given by

$$\tan 2\psi^E = \frac{2R \cos \alpha}{1 - R^2}, \quad \tan 2\psi^W = -\frac{2R \cos \alpha}{1 - R^2}.$$

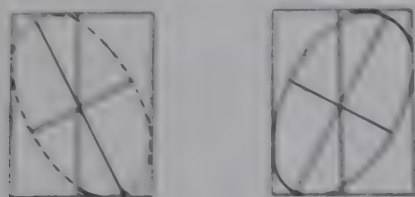


Fig. 6

It is easy to see that $\psi^E = (\pi + \frac{1}{2})\pi - \psi^W$. These ellipses can be shown to be inscribed within oblongs having the sides

$$\left(\pm \frac{C}{\sin \alpha}\right), \quad \left(\pm \frac{C}{R \sin \alpha}\right)$$

and touching the sides at the points

$$(\pm C_{r,w} \sin \alpha), (\mp C_{r,w} \cot \alpha / R); (\pm C_{r,w} \cot \alpha), (\mp C_{r,w} \frac{\sin \alpha}{R}). \quad (2.17a)$$

The ratio of the axes is given by

$$\frac{(1 + R^2) \pm \sqrt{1 - R^2 - 4R^2 \sin^2 \alpha}}{(1 - R^2) \pm \sqrt{1 - R^2 - 4R^2 \sin^2 \alpha}}.$$

From these general expressions we can obtain the shape and sense of rotation of the polarisation ellipse at any point inside the ionosphere. We have described the nature of

polarisation of the electric vector for any value of ξ , the last column of Table II.

§3. THE COUPLING TERM

Let us now turn to the application of these formulae to actual cases. For these, we require the characteristic ionospheric stations. These are given in Table III for number of stations between the geomagnetic equator and N.M.P.

The second row gives the propagation angle θ of stations given in the first row, and the other rows are self-explanatory. As we see from row 6, the value of the magnetic damping factor varies from ∞ at the equator to zero at the pole, passing through a value of 75×10^3 at the ionospheric station nearest to the G.M.-equator to 5.5×10^4 sec. at the Clyde River station which is nearest to the N.M.P.

The values of all ionospheric quantities R , α , ϕ , q , are functions of ξ and η . Now $\xi = v/v_0$ and is independent of ρ . The collision frequency in any ionospheric layer is taken to vary as $v = v_0 \exp \left\{ -\frac{z - z_0}{l} \right\}$, where l is the scale height, v_0 is the value of the collision frequency at the tip of the layer, z_0 is the height of the tip of the layer. The values of v_0 , z_0 vary with the hour of the day, the season and other factors. We have taken

$$v_0 = 2 \times 10^6 \text{ sec. for the E-layer,}$$

$$= 10^6 \text{ sec. for the F-layer.}$$

as good average values for v_0 .

TABLE III

	Equator	Huancayo	Calcutta	Singh	Norina	Clyde River	North Pole
θ	90°	92°	112°	137°	167°	174°	180°
$\frac{1}{(H)}$		-296 Γ	-494 Γ	-470 Γ	-514 Γ	-570 Γ	
$f_h = \frac{cH}{2\pi m v}$		-829.10°	1.222.10°	1.316.10°	1.439.10°	1.596.10°	
$\Omega = \frac{\sin^2 \theta}{2 \cos \theta}$	∞	14.31	1.148	0.63	0.26	-0.05	0
$1/v_0 l = 2\pi/f_0 \Omega$	∞	74.50.10°	8.79.10°	6.86.10°	153.10°	-0.53.10°	0
$v = 2.10^6$	0	-269.10 ⁻³	2.27.10 ⁻²	29.2.10 ⁻³	84.8.10 ⁻³	364.10 ⁻³	∞
$ \xi = \frac{v}{ v_0 }$							
$v = 10^2$	0	-134.10 ⁻⁴	1.14.10 ⁻⁴	14.6.10 ⁻⁴	42.6.10 ⁻⁴	182.10 ⁻⁴	∞
$v = 2.10^3$	0	-200.10 ⁻³	1.71.10 ⁻³	28.9.10 ⁻³	227.10 ⁻³	22.7.10 ⁻³	∞
$l = 10 \text{ km.}$							
$v = 10^3$	0	-040.10 ⁻³	-341.10 ⁻³	4.37.10 ⁻³	12.8.10 ⁻³	55.6.10 ⁻³	∞
$l = 50 \text{ km.}$							

The corresponding values of ξ_0 are given in rows (7) and (8), for the E and F layers.

We observe that for the F -layer, ξ_0 varies from $\approx 10^{-4}$ at sunrise to $1/8 \cdot 10^{-2}$ at Clyde River. We can therefore set $\xi \approx 1$ for F -layer propagation. At the G.M.F. = 0, and at the pole $\xi = \infty$. These points require separate treatment. For the treatment of wave propagation through layer, we have therefore to confine ourselves to regions I and IV of the $\xi\eta$ -plane.

For the E -layer, ξ_0 continues to be small for low latitude stations, but at Clyde it has attained the value .25 and at times may approach unity. For the higher latitude stations, e.g. Clyde River $\xi_0 = 3.63$.

PATH OF THE RAY IN THE $\xi\eta$ -PLANE

The vertical propagation of a ray in the $\xi\eta$ -plane can be shown by a trajectory. We have

$$\xi = \xi_0 \exp \left\{ -\frac{z-z_0}{l} \right\} \quad (3.1a)$$

and

$$\eta = \frac{1}{\alpha_0} (1 - \gamma_0 \gamma)$$

where $\gamma_0 = \frac{4\pi N_0 \epsilon^2}{n \mu^2} = \beta^2 / \mu^2$ and

$$\gamma = \exp \left\{ \frac{1}{2} \left[1 - \frac{z-z_0}{l} - e^{-\frac{z-z_0}{l}} \right] \right\} \quad (3.1b)$$

is the Chapman Factor.

N_0 is the maximum concentration of ions in the layer.

Let us now consider the coupling coefficient ϕ . It can be easily shown that

$$\phi = 2\alpha_0^{-1}(\rho) = \frac{1}{2} \cdot \frac{1 - \xi^2}{1 - \xi^2 + \eta^2} - 2\eta\xi \quad (3.2)$$

We obtain after some work

$$R_e(\phi) = \frac{1}{2} \cdot \frac{1 - \xi^2 - \eta^2 \xi - 2\eta\xi\xi}{1 - \xi^2 + \eta^2 \xi^2 + 4\eta^2 \xi^2} \quad (3.3a)$$

$$I_m(\phi) = -\frac{1}{2} \cdot \frac{(1 - \xi^2 + \eta^2) \xi - 2\eta\xi\xi}{(1 - \xi^2 + \eta^2 \xi^2 + 4\eta^2 \xi^2)} \quad (3.3b)$$

$$|\phi| = \frac{1}{2} \left[\frac{1 - \xi^2}{1 - \xi^2 + \eta^2 \xi^2 + 4\eta^2 \xi^2} \right]^{\frac{1}{2}} \quad (3.3c)$$

Let us now find out values of η and ξ . With the assumptions made in this section, i.e. $r = r_0 \exp[-(z-z_0)/l]$ it can be easily shown that

$$\xi = \frac{d\xi}{du} = -\frac{\epsilon}{\rho} \frac{\eta}{1 + \eta^2}$$

Similarly it can be shown, assuming that N is given by a Chapman-layer, that

$$\eta = \frac{\alpha r}{\rho \beta_0 l} \beta = \frac{\epsilon}{\rho l} \beta \left(\frac{1}{\beta_0} - \eta \right)$$

where

$$\beta = \frac{1}{2} (1 - e^{-\epsilon \eta / \rho l})$$

We have therefore

$$R_e(\phi) = \frac{\epsilon}{2\rho l} \cdot \frac{(1 - \xi^2 - \eta^2 \xi - 2\eta\xi\xi) \beta \left(\frac{1}{\beta_0} - \eta \right) - 2\eta\xi\xi}{1 - \xi^2 + \eta^2 \xi^2 + 4\eta^2 \xi^2} \quad (3.4a)$$

$$I_m(\phi) = \frac{\epsilon}{2\rho l} \cdot \frac{(1 - \xi^2 + \eta^2 \xi + 2\eta\xi\xi) \beta \left(\frac{1}{\beta_0} - \eta \right)}{1 - \xi^2 + \eta^2 \xi^2 + 4\eta^2 \xi^2} \quad (3.4b)$$

$$|\phi| = \frac{\epsilon}{2\rho l} \left[\frac{\beta^2 \left(\frac{1}{\beta_0} - \eta \right)^2 + \xi^2}{1 - \xi^2 + \eta^2 \xi^2 + 4\eta^2 \xi^2} \right]^{\frac{1}{2}} \quad (3.4c)$$

From the above expression for $|\phi|$ it is seen that this attains its maximum value at $\eta = 0$. We have then

$$|\phi_{\max}| = \frac{\epsilon}{2\rho l} \cdot \left[\frac{\beta^2 \beta_0^2 + \xi^2}{(1 - \xi^2)^2} \right]^{\frac{1}{2}} \quad (3.5)$$

Therefore $|\phi_{\max}|$ is very large for $\xi \approx 1$ and tends to infinity as $\xi \rightarrow 1$.

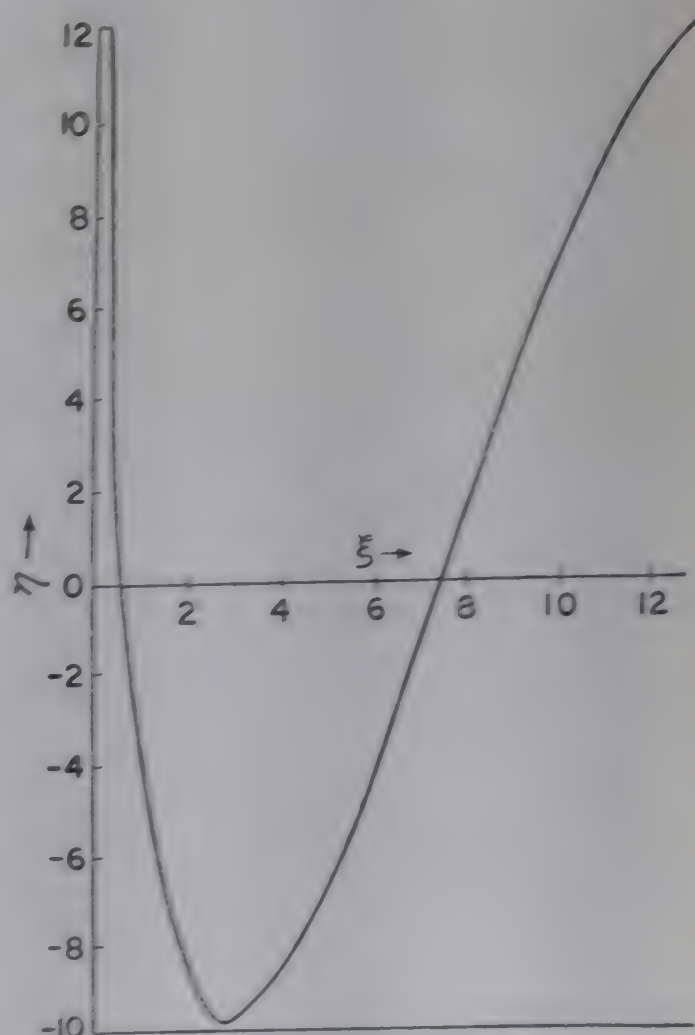


Fig. 7

When a wave of any frequency travels through a layer we observe that to every point of the layer there correspond definite values of ξ and η ; we can therefore plot on the $\xi\eta$ -plane a series of points corresponding to different values of z . The curves joining these points may be called the trajectory of the wave in the $\xi\eta$ -plane. Such a trajectory drawn for Slough is shown in fig. 7. The points ξ and η have been calculated on the assumption that the variation of collision frequency is given by (3.1a) and the electron concentration is given by (3.1b). As we are interested in the maximum value of ϕ , we require the value of ξ at $\eta=0$ on the trajectory of the wave in the $\xi\eta$ -plane. This value of ξ depends on the frequency of the wave and the location of the station. Fig 8 gives a number of (ξ, θ) curves (at $\eta=0$) for different values of p/p_c . The layer has been assumed to be the E -layer with $\nu_0=2.10^5/\text{sec}$. The corresponding values of ξ for an F -layer with $\nu_0=10^9/\text{sec}$. will simply be 1/200th of the values given by the curves.

Certain conclusions can be immediately reached from the nature of these curves.

The frequency at which the point $(\xi=1, \eta=0)$ is crossed depends on the magnetic characteristics of the station and the relation is given as

$$p = p_c (\nu_c / \nu_0)^{1/2} e^{-1/2\theta^2}$$

For stations where the magnetic damping is large compared to the collisional damping (equatorial region) this point is reached when $p \ll p_c$, while for high latitude stations $\nu_c \ll \nu_0$ and this critical value of p approaches p_c . For F -layer propagation, since $\nu_c \gg 1$ practically over the entire globe (excepting the small polar belt), it follows that the critical point $(\xi=1, \eta=0)$ will be reached when $p \ll p_c$, i.e. when the wave will fail to reach F -layer owing to the presence of the lower E -layer.

Only when $\nu_c/\nu_0 \approx 1$ cases of practical importance will arise. Ionospheric stations like Kiruna and Slough are

TABLE OF NOTATIONS

Quantity	Saha <i>et al.</i>	Appleton <i>et al.</i>	Hartree	Eckersley	Rydbeck
Direction of Propagation	z	z	..	z	z
Horizontal in Magnetic Meridian	x	x	..	x	y
Horizontal $\perp$ Magnetic Meridian	y	y	..	y	x
Propagation Angle	θ	..	..	..	θ
Field Vectors	E, H, P, D	E, H, P, D	L, H, D	$E, P,$	E, D, P
Earth's Magnetic Field	H	H	H	H	H
Refractive Index	μ	μ	μ	μ	μ
Complex Refractive Index	$q = \mu - i\kappa c/p$	μ	K	Z	μ
Absorption Coefficient	K	K	..	..	..
Pulsatance	p	p	κc	$2\pi\nu$	ω
Gyropulsatance $\frac{eH}{mc}$	p_h	p_h	$k_h c$	$2\pi\nu_H$	ω_H
Frequency	f	f	$\kappa c/2\pi$	ν	$\omega/2\pi$
Gyrofrequency	f_h	f_h	$k_h c/2\pi$	ν_H	$\omega_H/2\pi$
Collision Frequency	ν	ν	$2k_c$	ν_c	ν
Relative Gyrofrequency $f_h/f = p_h/p$	ω	$-\gamma, \alpha, \beta$	τ	τ	γ/x_0^2
Relative Collision Frequency ν/p	δ	..	..	$\alpha_c/2\pi$	δ
Phase Velocity	v	v	..	..	..
Group Velocity	w	w	..	..	..
Displacement of the Ion	$\vec{S}(\xi, \eta, \zeta)$	x, y, z	$\vec{P}$	..	..
Dipole Moment	$\vec{N}eS$	$Ne(x, y, z)$	NeP	..	..
Scattering Tensor	$\frac{\gamma\Delta}{\beta(\beta^2 - \omega^2)}$	..	σ	$-\alpha$	..
Ratio of Axes	ρ	R	..	..	..
Critical Pulsatance $\frac{4\pi Ne^2}{m}$	p_c^2	p_c^2	..	$4\pi^2\nu_0^2$	α_c^2
$4\pi Ne^2/m p^2 = \rho^2/p^2$	r	$-\frac{1}{\alpha}, x$	σ_0	ζ	$\frac{1}{x_0^2}$
$\frac{eH}{mc p} [1 - i\nu/p]$	$-\omega/\beta$	..	$K\alpha H$	ν_H/ν'	..
$\frac{4\pi Ne^2}{m p^3} / (1 - i\nu/p) [1 - p_h^2/p^2 (1 - i\nu/p)^2]$	$-4\pi A/\beta^3$	$\frac{\alpha}{\alpha^2 - \gamma^2}$	ξ	ζ	..
$\frac{4\pi Ne^2}{m p^3} / [1 - i\nu/p]$	r/β	$\frac{1}{\alpha + \alpha}$	σ_0	..	..
$m p \nu / 4\pi Ne^2$	δ/r	β	..	..	..
$\frac{m p}{4\pi Ne^2} \left[\frac{eH}{mc} \right]$	$\frac{\omega}{r}$	γ	P/σ_0	..	γ

therefore suitable for observations of any peculiarities arising out of this coupling term. In such cases $|\dot{\phi}|_{\max}$ will be quite large and the approximate differential equations

cannot be denied that the nature of propagation may be profoundly modified. As no one has yet been able to give an exact treatment of the differential equations, it is not safe to make any definite statement about the nature of this modification.

ACKNOWLEDGMENT

B. K. Banerjee wishes to record his thanks to the National Institute of Sciences for the award of a Fellowship. U. C. Guha wishes to record his thanks to the Council of Scientific and Industrial Research for the award of a scholarship.

REFERENCES

- BANERJEA, B. K. (1947). Propagation of e.m. waves in the upper atmosphere. *Proc. Roy. Soc. A.*, **196**, 67.
 BOOKER, H. G. (1934). Some general properties of the Formulae of the Magneto ionic theory. *Proc. Roy. Soc. A.*, **150**, 267.
 EPSTEIN, P. S. (1930). Reflection of waves in an inhomogeneous absorbing medium. *Proc. Nat. Acad. Sci.*, **16**, 629.
 FÖRSTERLING, K. (1942). Über die Ausbreitung elektromagnetischer Wellen in einem magnetisierten Medium bei Senkrechter Inzidenz. *Hochfrequenztechnik U. Elektroak.*, **A**, **95**, 546.
 HARTREE, D. R. (1929). Magnetoionic propagation of e.m. waves in the ionosphere. *Proc. Camb. Phil. Soc.*, **25**, 47.
 RAWER, K. (1939). Elektrische Wellen in einem geschichteten Medium. *Ann. d. Phys.*, **35**, 402.
 RYDBECK, O. E. H. (1942). The reflection of e.m. waves from a parabolic friction free ionized layer. *Jour. Appl. Phys.*, **13**, 577.
 RYDBECK, O. E. H. (1950). Triple splitting in the ionosphere. *Proc. Nat. Acad. Sci.*, **4**, 329.
 SAHA, M. N. and RAI, R. N. (1937). Propagation of e.m. waves through the atmosphere. *Proc. Nat. Inst. Sci. (India)*, **III**, **3**, 359.
 SAHA, M. N., BANERJEA, B. K. and GUHA, U. C. (1947). Propagation of e.m. waves through the ionosphere. *Ind. Jour. Phys.*, **4**, 181.
 SCOTT, J. C. W. (1950). Longitudinal and Transverse propagation. *Jour. Geo. Phys. Res.*, **55**, 64.

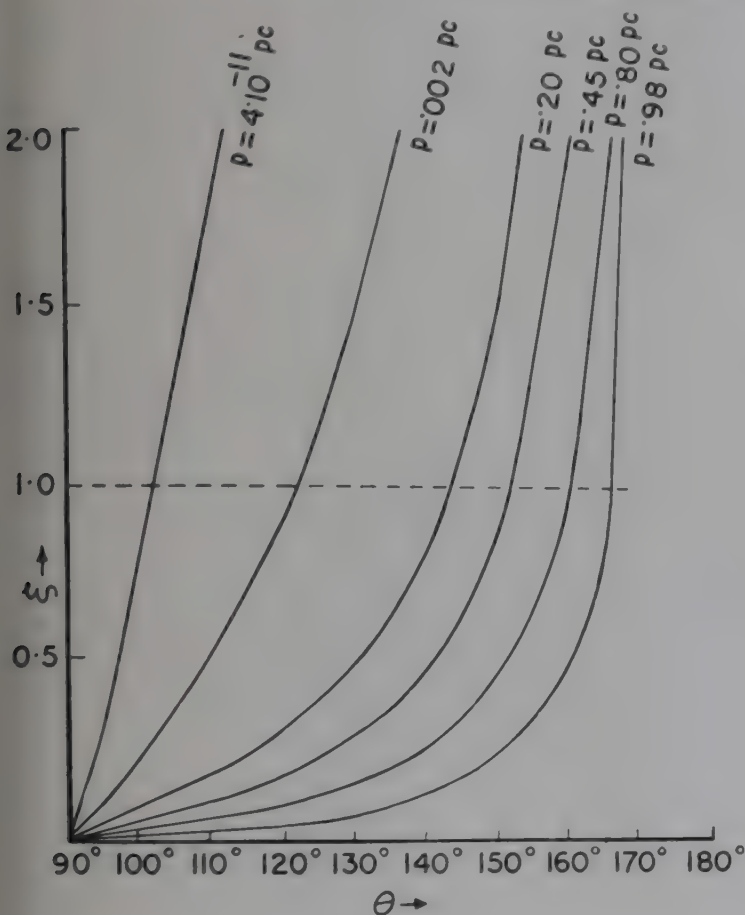


Fig. 8

will no longer be valid. Though this does not necessarily imply that the large $|\dot{\phi}|$ is solely responsible for the triple splitting, as has been suggested by Rydbeck, it

86. OCCURRENCE OF STRIPPED NUCLEI OF NEON IN PRIMARY COSMIC RAYS

(*Nature*, **167**, 476, 1951)

Bradt and Peters, in their analysis of the primary cosmic radiation as observed in the out-of-the-atmosphere observations with the plate technique, have given the completely stripped nucleus of neon as one of the main components of the heavier cosmic particles. In fact, the relative abundance is given as almost the same as that of oxygen-16 (*vide* Fig. 13, p. 66, of their paper).

It appears that if the identification of the stripped nucleus of neon as one of the main constituents of primary cosmic particles be correct, and is confirmed by subsequent

observations, it constitutes a very strong argument against the hypothesis that the sun is the source of cosmic particles received on the earth^{2,3}. For to have stripped nuclei of neon from the sun, it must be first demonstrated that neon exists on the sun and is at least once ionized on the photosphere or the chromosphere. The evidence on these points, as will be shown presently, is absolutely negative, in spite of the fact that strong lines of Ne and Ne⁺ occur within the solar range of wave-lengths (3,000-10,000 Å.)

It is true that the fundamental lines of Ne and Ne^+ occur in the far ultra-violet, and the lines which occur in the solar range belong to the transitions:

$$\begin{aligned} &1s^2.2s^2 (2p^5.3s-2p^5.3p) \text{ or higher transitions for Ne} \\ &1s^2.2s^2 (2p^4.3s-2p^4.3p) \text{ or higher transitions for Ne}^+ \end{aligned} \quad (A)$$

But the physical conditions on the sun, as we know, are such that if neon existed there at even moderate strengths the lines of Ne, Ne^+ belonging to the above-mentioned combinations could not escape detection, at least in the flash spectrum of the sun. An analogous case is afforded by He and He^+ , which have their fundamental lines in the extreme ultra-violet; but of the higher transition lines, only λ 10,830.38, $1s.2p^3S_1-1s.2p^3P_1$ is found as an absorption line in the Fraunhofer infra-red spectrum⁴; and none of the other lines of He, $1s.(2s^1.3S-np^1.3P)$, $1s.(2p^1.3P-nd)$, is found ordinarily in the Fraunhofer spectrum, except when the solar atmosphere is disturbed. But the lines $1s.2p^1.3P-1s.nd^1.3D$, which include the well-known D_3 and other higher transition lines of helium, are found in great strength in the solar chromosphere; thus proving that though helium exists in great strength in the higher solar atmosphere, it is difficult of observation in the Fraunhofer spectrum owing to the large excitation potential of its excited levels, which can give rise to Fraunhofer lines by absorption. But determinations of the abundance of helium to hydrogen in the chromosphere can be obtained on certain plausible assumptions, and are variously given as 1 : 14, 1 : 33, etc.

The presence of ionized helium in the flash spectrum is indicated through the line λ 4,685.91, $\nu=4N \left(\frac{1}{3^2} - \frac{1}{4^2} \right)$. This is unexpected, on account of the high ionization potential of helium (24.465 volts), and the extra excitation required to raise normal He^+ to the 4-quantum levels. The physical mechanism producing He^+ in the chromosphere is still unknown, and the reader may be referred to a suggestion which I myself have made⁵.

If neon were present at some strength in the sun, we could expect, from analogy with helium, that lines of both Ne and Ne^+ would be present in the flash spectrum of the sun. But, in spite of laborious attempts, not a single coincidence of the numerous lines of Ne and Ne^+ belonging to combinations (A) could be found in the table of the flash-spectrum of the sun published by Menzel⁶ (1931)

or Mitchell⁷ (1947). We must, therefore, conclude that both Ne and Ne^+ are definitely absent from the atmosphere of the sun.

So far as I know, no lines of neon or of any inert gas except helium have been found in the spectra of stars belonging to the main sequence. Forbidden lines of Ne^{2+} , Ne^{3+} , Ne^{4+} are found in the spectra of the nebulosity which is formed from gases ejected by a nova, and lines (A) of Ne and Ne^+ have been found in certain B- and A-stars, which show abnormal characteristics like τ -Scorpii. These form less than 10^{-4} times the number of stars the spectra of which have been examined, and we are therefore driven to the conclusion that occurrence of Ne and Ne^+ in these rare bodies is due to some extraordinary cosmogenic process. The attempt of Harrison⁸ to prove the existence of neon in the interior of the sun from opacity data is inconclusive, as his arguments can equally well apply to neighbouring elements like fluorine or sodium.

There is therefore at present no positive evidence of the presence of Ne or Ne^+ in the sun or the usual run of stars, and this is a strong point against the hypothesis of the solar origin of our local primary cosmic ray particles. The theories which ascribe a high cosmic abundance to neon are not borne out by stellar data.

I wish to express my indebtedness to Dr. B. Peters for discussion of these points during the conference on elementary particles held at Bombay in December 1950, under the auspices of the Tata Institute of Fundamental Research.

Institute of Nuclear Physics,
Calcutta University, Jan. 17.

¹ Bradt and Peters, *Phys. Rev.*, **77**, 54 (1950).

² Richtmeyer and Teller, *Phys. Rev.*, **75**, 1729 (1948).

³ Alfvén, *Phys. Rev.*, **75**, 1732 (1948).

⁴ Babcock, "The Solar Spectrum (λ 6,600 to λ 13,495 Å.)" (Carnegie Institution of Washington).

⁵ *Proc. Phys. Soc., Lond.*, **57**, 271 (1945).

⁶ Menzel, Pub. Lick Observatory, Calif. (1931). *Trans. Inter. Astro. Union*, **7**, 471 (1950).

⁷ Mitchell, *Astrophys. J.*, **105**, 1 (1947).

⁸ Harrison, *Astrophys. J.*, **108**, 310 (1948).

Unsöld, "Physik. der Sternatmosphäre", 416 (1938).
Unsöld, *Z. Astrophys.*, **24**, 1, 22, 229 (1942).

87. DETERMINATION OF THE ELECTRON CONCENTRATION AND THE COLLISION FREQUENCY IN THE IONOSPHERE LAYERS OF THE O AND X WAVES*

Proc. Mixed Commission on the Ionosphere, Brussels, 211, 1954

ABSTRACT

It is well-known that according to the ray-theory, the O and X waves reflected from different layers of the ionosphere would be ellipses, with their major axes tilted at an angle ψ to the geomagnetic N-S axis, and the ratio of the axes (b/a) varying from one at the GM poles to zero at the GM equator. These deductions are also confirmed from the wave theory, particularly for stations of low latitudes; for higher latitudes, the wave coupling factor may not be negligible. Experimental studies of the polarization characteristics of the downcoming waves have been so far mostly confined to high latitudes. The patterns are found to be nearly circular ($b/a \simeq 1$), and it is difficult to measure the tilt angle accurately. There are in fact very few measurements for intermediate latitudes, where there is possibility of accurate measurement of the tilt angle and of getting a value of (b/a) different from one and zero.

This subject has been discussed by R. Roy and J. K. D. Verma from the wave theory of propagation in the form given by Saha, Banerjee and Guha (1951), and it has been shown that it is possible to deduce from the values of ψ and b/a the electron concentration and the collision frequency in the ionospheric regions from which the waves are reflected.

The mathematical work needed for these calculations may be briefly given here. We introduce two quantities:

$$\xi = \nu/\nu_c, \quad \eta = (1-r)p/\nu_c$$

where ν_c is the critical collision frequency of Appleton, viz., $\nu_c = -\frac{|p_n|}{2 \cos \Theta} \cdot \sin^2 \Theta$, Θ being the angle of propagation varying from zero in the south G. M. pole to π in the north G. M. pole, ν is the collision frequency, $r = \frac{4\pi N e^2}{m p^2}$, N being the electron concentration, and p the pulsantance of the exploring wave.

It has been shown (Saha *et al.*, 1951) that the electric field intensity of the exploring wave is split up into two given by:

$$\frac{E_x + i\rho_1 E_y}{\sqrt{1 + \rho_1^2}} \quad \text{and} \quad \frac{E_x + i\rho_2 E_y}{\sqrt{1 + \rho_2^2}}$$

where:

$$\rho_1 = G - \sqrt{1 + G^2}, \quad \rho_2 = G + \sqrt{1 + G^2}, \quad G = 1/(-\eta + i\xi)$$

the waves being propagated with the velocities cq_0 and cq_x where q_0 and q_x are the refractive indices of the O- and X-waves given by the ray theory.

We can put:

$$i\rho_1 = R e^{i\alpha}, \quad i\rho_2 = R^{-1} e^{-i\alpha}.$$

To obtain the values of R and α , we make use of a ξ - η plane, covering all the characteristics of the ionosphere. It may be called the characteristic plane.

The values of R and α may be obtained with the aid of the following formulae:

$$\left(\frac{\xi}{\xi^2}\right)^2 \cdot \left(\frac{2R}{1+R^2}\right)^2 + \left(\frac{\eta}{\eta^2}\right)^2 \cdot \left(\frac{2R}{1-R^2}\right)^2 = 1$$

$$\frac{(\xi/\xi^2)^2}{\cos^2 \alpha} - \frac{(\eta/\eta^2)^2}{\sin^2 \alpha} = 1$$

or,

$$\frac{\xi^2}{2} \sin^2 2\alpha + \cos 2\nu + \cos 2\alpha = 0$$

where:

$$\zeta^2 = \xi^2 + \eta^2, \quad \text{and} \quad \nu = \tan^{-1} (\xi/\eta).$$

The reader can verify that the above relations hold even if R is changed to $1/R$, or α changed to $-\alpha$. The R =constant and α =constant curves in the ξ - η plane have been shown in fig. 1. Though only the values of $R < 1$, and positive values of α have been shown, the R =constant, and α =constant curves hold for R^{-1} and $-\alpha$ as well.

These ambiguities have been cleared by detailed discussions on the polarization factors:

$$\rho_1 = G \{1 - \sqrt{1 + 1/G^2}\}, \quad \rho_2 = G \{1 + \sqrt{1 + 1/G^2}\}$$

in which $\sqrt{1 + 1/G^2} = \{(1 - \xi^2 + \eta^2) - 2i \xi \eta\}^{\frac{1}{2}}$ can have two signs. For the case of the northern hemisphere where $\xi > 0$, the values of R and α are shown in figure 2. It is seen that the ξ - η plane is divided into four sections by the lines $\eta = 0$, $\xi = 1$. For a place like Calcutta where $\nu_c = 3.66 \times 10^6$, ξ is less than 1, the wave coupling factor may be neglected, and the split waves are confined to the region I for ν as high as 10^6 .

*This reports the work done by Mr. B. M. Banerjee, Mr. R. Roy and Mr. J. K. D. Verma at the Institute of Nuclear Physics, Calcutta.

It is found that for the O and X waves, the electrical field intensities satisfy the relations:

$$\text{O wave} \rightarrow E_x^2 + 2R \cos \alpha E_x E_y + R^2 E_y^2 = C_0^2$$

$$\text{X wave} \rightarrow E_x^2 + 2R^{-1} \cos \alpha E_x E_y + R^{-2} E_y^2 = C_x^2$$

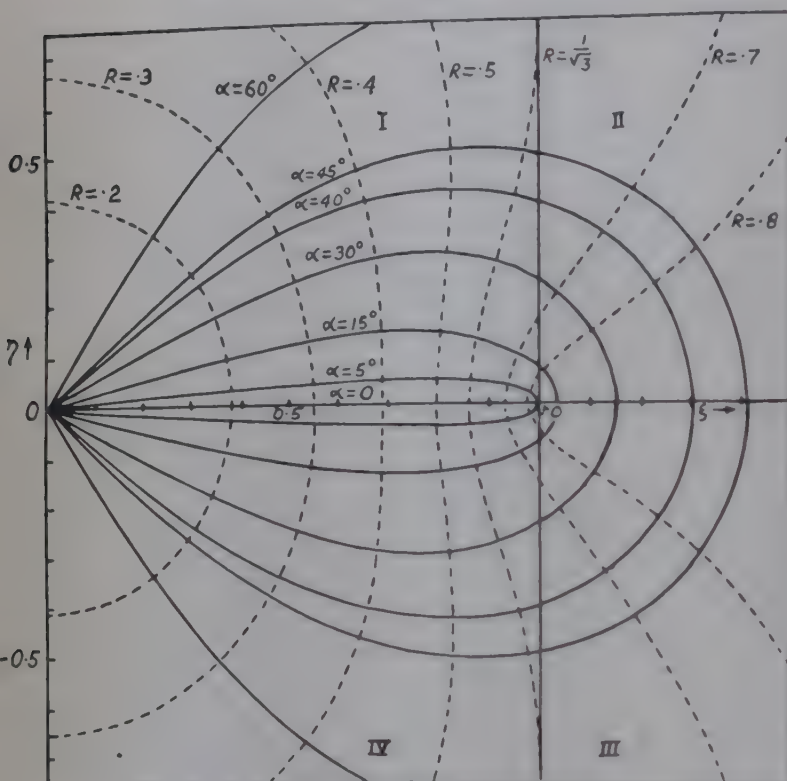


Fig. 1

From these relations, it is easily deduced that the polarization patterns would be ellipses tilted with respect to the x axis (N-S) through the angles ψ given by:

$$\tan 2\psi_0 = \frac{2R \cos \alpha}{1-R^2}, \quad \tan 2\psi_x = -\frac{2R \cos \alpha}{1-R^2}$$

It has not been found possible to determine from theoretical considerations, the level to which the limiting polarization of the downcoming waves should correspond. It may be noted that the downcoming waves would appear with the characteristic polarization corresponding to some level in the ionosphere of particular electron density and collision frequency. If after reflection, the waves travel without any change of phase velocity, the polarization factors and hence the values of R and α will correspond to the levels of ionization in the layer from which the waves had been reflected. The values of R and α are obtained from the experimental results as follows: it can be shown that:

$$x = \frac{\text{minor axis}}{\text{major axis}} = \frac{b}{a} = \frac{\{1 + R^2 - \sqrt{1 + 2R^2 \cos 2\alpha + R^4}\}^{\frac{1}{2}}}{\{1 + R^2 + \sqrt{1 + 2R^2 \cos 2\alpha + R^4}\}^{\frac{1}{2}}}$$

$$y = \tan 2\psi_0 = \frac{2R \cos \alpha}{1-R^2}.$$

from which the following relations can be deduced:

$$R = \left\{ \frac{\sqrt{1+y^2}(1+x^2) - (1-x^2)}{\sqrt{1+y^2}(1+x^2) + (1-x^2)} \right\}^{\frac{1}{2}}$$

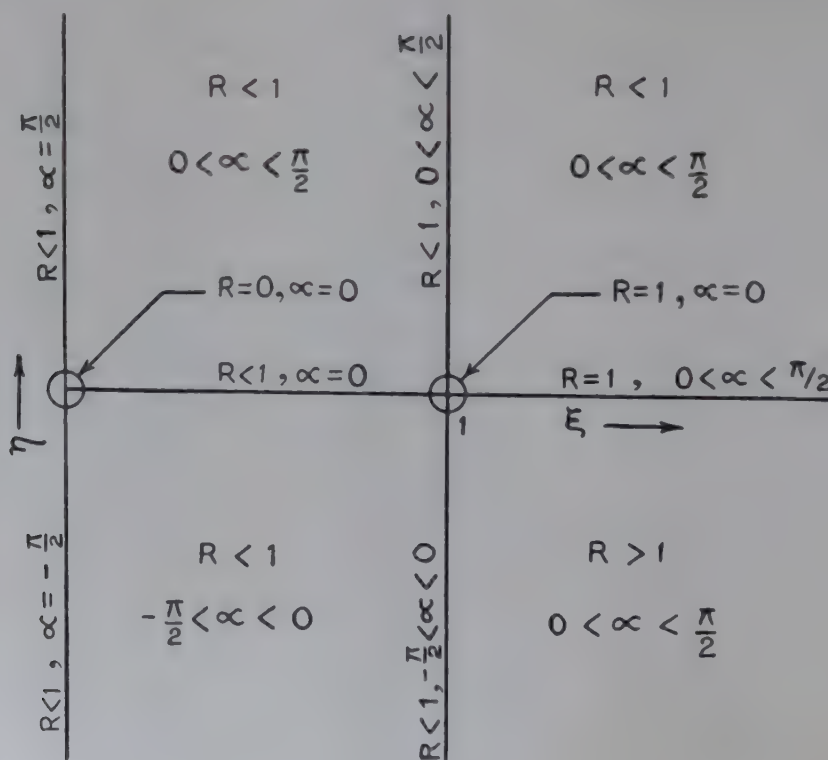


Fig. 2

$$\cos \alpha = \frac{y(1-x^2)}{[(1+y^2)(1+x^2)^2 - (1-x^2)^2]^{\frac{1}{2}}}$$

From the values of R and α , we deduce:

$$\tan \nu = \xi/\eta = \frac{i+R^2}{1-R^2} \cot \alpha,$$

$$\eta^2 + \xi^2 = -\frac{2(\cos 2\alpha + \cos 2\nu)}{\sin^2 2\alpha},$$

then we have:

$$\eta = \frac{(1-r)p}{\nu_c} = (\xi^2 + \eta^2)^{\frac{1}{2}} \cos \nu,$$

$$\xi = \frac{\nu}{\nu_c} = \eta \tan \nu.$$

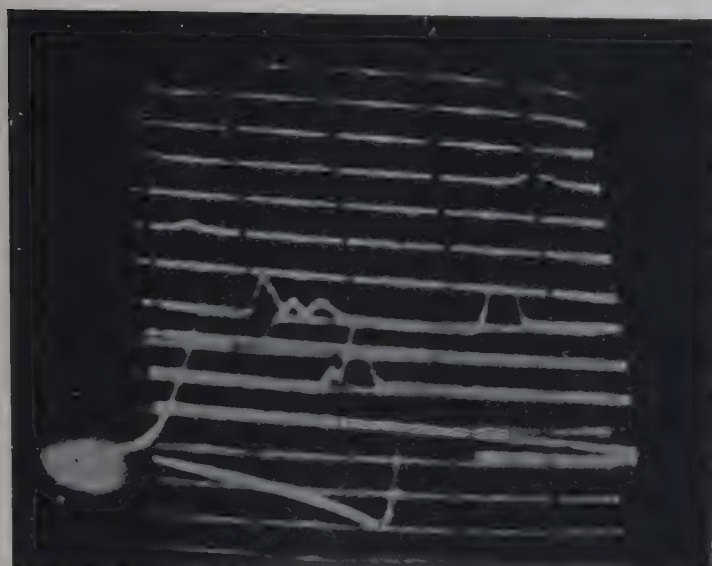


Plate I

Type A display of echoes from the ionosphere at 2.9 Mc/s (recorded at 1652 hours IST on 1-1-53). The raster sweep of twelve lines are executed from right to left (the faint lines are due to the other beam of the CRO), and each line corresponds to 50 kms. of equivalent height and there are markers (bright and dark spots) at intervals of 5 kms.

Line	Height km	Remarks
1	—	Ground Pulse
3	108.5	E _s Cloud
3	111.5	E _s Thin layer type
5	197	F _o
5	212	F _s Cloud
5	215	F _s Cloud
5	217.5	F _x
7	323.5	(E _s + F _s)
9	388.5	F _s Cloud

The echoes due to scattering from electron-clouds embedded in E and F layers are transitory and rarely persist for more than two minutes.

These results will be useful, if good experimental methods for the accurate measurement of ψ_0 and b/a , can be found.

So far the experimental studies have suffered from two handicaps, viz.,

(a) On account of insufficient resolution, it is not often possible to separate the O- and X-waves sufficiently,

(b) The intensities of the reflected beams undergo rapid fluctuations due to the superposition of waves scattered at small angles by moving electron clouds.

The difficulties have been overcome by the design of a new type of ionospheric recorder (Banerjee and Roy, 1950, 1952) using two principles viz.,

(a) Use of a short duration exploring pulse 6-30 μ seconds in place of the usual pulse of 100-200 μ seconds, with suitably designed receiving systems,

(b) Use of a raster-sweep time base of twelve lines, each corresponding to 50 km of equivalent height. It is then possible to obtain a resolving limit of 2 km.

Experiments with this recorder have shown that it is possible to separate the reflected O- and X-waves (Plate I) completely from the scattered waves due to irregularities like moving electron clouds (Roy and Verma 1953). Distinct pips corresponding to all these waves appear on the CRO screen, but while the O- and x-wave pips are fairly steady in position and intensity, the pips owing their origin to scattered waves fluctuate in position and intensity. The echoes for each type of wave, can therefore be picked up and studied separately.



Plate II

(A) Polarization pattern of the σ -wave.

(B) Polarization pattern of the x -wave.

Recorded at 12 noon IST on 9.3.54 at 5.45 Mc/s.

The state of polarization of these resolved echoes were studied by Roy and Verma with the help of a radio polarimeter following Eckersley's method of echo-selection. The O- and X-waves always come as tilted ellipses and with an axis ratio of approximately 2 to 4, and the sum of their tilt angles is 270° . It is difficult to obtain the polarization patterns of scattered waves. They come sometime as circles, sometime as tilted lines and sometime as ellipses. Not much study has been made of them yet.

To elucidate how N and ν are determined from the polarization data, the results of a typical observation for the F2-layer echoes are given in (Plate II).

O- ellipse: $\alpha=2$, $\psi_o=119^\circ$

X- ellipse: $\alpha=32$, $\psi_x=150^\circ$

So $\psi_o + \psi_x = 269^\circ \simeq 270^\circ$ as theoretically expected. We obtain by the use of the formulae:

$R = .5856$, $\alpha = 26^\circ 3'$ for the O- wave.

$\tan \nu = 4.182$, $\xi^2 + \eta^2 = .891$, $\eta = .2196$, $\xi = .9183$

from which we get $r=.98$, $\nu=3.07 \times 10^6$, and for the x-wave similarly r is found to be .95 and $\nu=3.55 \times 10^6$. Polarization patterns of the echoes from the E-layer show that they correspond to a value $r=1$, and $\nu=1.72 \times 10^6$. It is to be noted that the limiting polarization of the waves correspond to the reflection level which leads to the conclusion that after reflection the waves are propagated without any change of phase velocity.

The experiments are still in the preliminary stage, but sufficient results have been obtained which convince us of the great potentialities of the method.

REFERENCES

1. M. N. SAHA, B. K. BANERJEE and U. C. GUHA.—*Proc. Nat. Inst. Sci., India*, **17**, 205, 1951.
2. B. M. BANERJEE and R. ROY.—*Ind. J. Phys.*, **24**, 411, 1940.
3. B. M. BANERJEE and R. ROY.—*Ind. J. Phys.*, **26**, 473, 1952.
4. R. ROY and J. K. D. VERMA.—*J. Geophys. Res.*, **58**, 473, 1953.

88. ON ELECTRON-CHEMISTRY AND ITS APPLICATION TO PROBLEMS OF RADIATION AND ASTROPHYSICS*

(*Jour. Astro. Soc. Ind.*, **10**, 72, 1920)

Read on the 6th July, 1920.

Both classical and modern Thermodynamics have hitherto been confined to the treatment of the influence of heat on material substances up to the stage of chemical decomposition and vaporisation (or atomisation). The successive stages which come up for treatment can be thus schematically written:-

Phase	Phenomenon	Example
Solid	Liquefaction	Ice
Liquid		
Gas	Vaporisation	Water
(Consisting of molecules)		
Gas	Decomposition	H_2O (Steam)
(Consisting of constituent atoms).		
Gas	Atomisation	H_2O_2
(Elementary)		
		H, O

* An introduction and synopsis of the following four papers communicated to the Phil. Mag.

Paper A. Ionisation in the Solar Chromosphere.

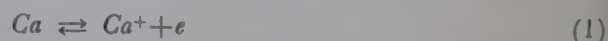
B. On the Problems of Temperature-Radiation of Gases.

C. On Elements in the Sun.

D. On the Harvard Classification of Stellar Spectra.

What happens when the gaseous mass consisting purely of atoms is further heated? The problem has not merely an academic interest, for though the temperatures we are considering may not be commanded in the Laboratory, such is usually the case in the Stellar universes with which we are acquainted through their spectra.

The answer to the problem raised easily follows from considerations of the Rutherford-Bohr theory of the atom viz., further heating of the gaseous mass will cause ionization i.e. some of the atoms will lose one electron, and under particular conditions of temperature and pressure, a definite chemical equilibrium will be established between the neutral atoms, the atoms which have lost one electron and the electrons split off, according to the scheme



That this will be the case may be seen from the fact that at high temperatures, many metals throw off copious quantities of electrons in these substances (Tungsten for example), ionization precedes liquefaction, just as in camphor, carbon and other volatile substances, vaporization (sublimation) precedes liquefaction.

These problems were foreshadowed by Nernst in his book

"Das Neue Warmesatz", for in page 154, we come across the following passage:-

"Die thermische Dissoziation eines Atoms in das positive Ion und das negative Electron ist also eindeutig bestimmt wenn wir die Dissoziationwärme kennen. Letzere ist in gewissen Fällen durch das Bohrsche Atommodell gegeben, wenn freilich dieser Weg zurzeit auch noch einigermassen hypothetisch ist".

The equation of chemical equilibrium of the process (1) is given by Nernst's law of Reaction-isochore,

$$\log K = \log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \log T \frac{\sum \gamma C_p}{R} + \frac{\sum \gamma C}{R}$$

Where x is the fraction of the total number of atoms dissociated,

U = heat of ionisation, in the energy-relation $\text{Ca} = \text{Ca}^+ + e - U$,

$\sum \gamma C_p$ = Sum of the atomic specific heats of the reacting atoms including the electron,

$\sum \gamma C$ = Sum of the chemical constants of the reacting atoms including the electron.

As suggested by Nernst, the specific heat at constant pressure of the electron is $\frac{5}{2} R$ (assuming the electron to be a monatomic gas) and its chemical constant can be calculated from the Tetrode-Sackur formula

$$C = -1.6 + \frac{5}{2} \log M,$$

if we put M , the atomic weight of the electron = $\frac{1}{1836}$. Eggert assumes the chemical constant of Ca and Ca^+ to be equal.

The formula finally stands as

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5.$$

The value of U still remains undetermined. At this place, Nernst's suggestion is entirely misleading, for the ionisation-potential of elements as determined by Franck and Hertz, Mackenand and others gives us the most exact data for the calculation of U , and it is unnecessary* to introduce any artificial hypothesis for calculating U , as Eggert has done.

The ionization-potential gives us the amount of energy which is required for tearing the outer-most electron from an atomic system to infinity. The quantity U (heat of ionisation for a gm-atom) can therefore be calculated from the relation,

$$U = \frac{eVN}{300J}, \quad N = \text{Avogadro Number}, \quad J = \text{Mechanical Equivalent of Heat}.$$

In cases where the ionisation-potential is not known, its value can be calculated from spectroscopic data from the value of $(1, s)$ which is the convergence-frequency of the

Principal series of the element, according to the quantum-relation,

$$V = \frac{h(1, s)}{e} \times 300$$

With the aid of equation (1), we can calculate and tabulate the degree of ionisation of the following elements at definite temperatures and pressures:—

Mg , Ca , Sr , Ba , Na , K , Rb , Cs — H , He . For other elements we have no satisfactory data.

Tables of percentage ionisation have been prepared from formula, and successfully applied to the following astrophysical problems.

(1) Occurrence of Elements in the sun and stars.

It has been shown that the alkali metals Rb , Cs are almost completely ionised in the sun, and hence cannot be detected by their ordinary lines. The lines of their ionized atoms lie in the ultra violet. K (I. P = 4.32 Volt) is 80% ionized, and hence is only feebly represented. Na (I. P = 5.12 Volt) is 60% ionized on the photosphere, but the ionization becomes complete when the pressure falls to 10^{-3} to 10^{-4} Atms and hence the D-lines are confined to the lower layers of the chromosphere. In the sunspots, temperature being diminished to about 5000°K , the ionisation falls down to 5% and hence the D-lines are greatly intensified.

(2) The occurrence of Enhanced lines in the chromosphere.

Of the alkaline earths, Ca is 30% ionized, while Sr and Ba are 50% and 60% ionized respectively. Hence on the photospheric level, we get not only the lines of Ca , Sr , and Ba , also of Ca^+ , Sr^+ , Ba^+ , but at greater heights, owing to the fall of pressure, ionization becomes almost complete. This explains the disappearance of the g-line of Ca , and of the corresponding lines of Sr and Ba , and exclusive occurrence of the enhanced lines in the high-level chromosphere. The case of the Mg -lines is also successfully treated. (With the aid of the following formula which represents the degree of dissociation for diatomic molecule.)

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{2.3RT} + \frac{5}{2} \log T + \sum \gamma C$$

it is shown, that H_2 and O_2 are completely dissociated into atoms not only in the sun, but also in sunspots, and are represented by their atomic spectra only. N_2 may remain partly undissociated and hence show its molecular spectrum (the so-called cyanogen band).

A method for dealing with the spectra of chemical compounds is also fore-shadowed.

(3) It is shown from considerations of the Bohr-Sommerfeld theory of spectral emission that the transition of an atom from a neutral state to the ionized state is not abrupt, but is marked by successive states of equilibrium of the atomic system. In the normal state, the system has the energy $A - h(hs)(1, s)$, corresponding to the possession of

* Eggert's object was to verify Eddington's hypothesis of ionisation in the interior of stars.

one quanta of angular momentum by the outermost vibrating electron. The next stable states of the atom are marked by the energy-contents A-h(2,p), A-h(3,d) etc. . . corresponding to the possession of 2, 3-m quanta of radial angular momentum by the vibrating electron. Ionisation corresponds to $m = \infty$.

It therefore follows that radiation of normal lines will precede ionisation, and the order in which the lines will come out is as follows:—

$$(1, s) - (m, p), (2, p) - (m, d), (3, d) - (4, b) \text{ etc} \\ (2, s) - (m, p), \text{ etc}$$

The temperature of emission of a certain group of lines therefore bears a relation to the temperature of ionisation of the atom, the general rule being that the higher the temperature of complete ionisation, the higher is the temperature at which the gas can be made to glow. It was shown that the existing data on radiation of elements under a purely thermal stimulus can best be explained on the above hypothesis. Thus while elements like Ca possessing a low ionisation potential can be excited even in the flame, even the highest temperatures fail to excite H_2 , O_2 , N_2 , A, which have very high ionisation-potentials varying from (13.6 to 25.6 volts). In the case of hydrogen, the temperature of complete ionisation is about $22000^\circ K$, and the temperature of emission for the Balmer lines is not less than $4500^\circ K$. The corresponding figures for Helium are $35000^\circ K$ and $12000^\circ K$.

(4) The second stage ionisation of elements.

If $P=1$ Atms, Ca becomes completely ionised when $T=13000^\circ K$. Beyond this stage, we have only Ca^+ atoms. But this now begins to get further ionised. A theory of this second-step ionisation is also worked out. The formula is approximately

$$\log \frac{x^2}{(2+x)(1-x)} = -\frac{U}{2.3RT} + \frac{5}{2} \log T - 6.5$$

With the aid of this formula, the second-step ionisation of Ca, Sr, Ba, Mg, He have been calculated.

Phenomena	Temp.	Press	Remarks	Stellar-class
Appearance of K	5000°	1 Atm	Beginning of the Ionisation of Ca	Ma
Disappearance of G	13000°	"	Ca completely ionised	
Appearance of Mg (4481)	7500°	"	Beginning of the Ionisation of Mg	B 8
Disappearance of K	19000°	"	Ca^+ completely ionised	
" of 4481	23000°	"	Mg^+ "	Od
Appearance of He	16000°	"	Beginning of the Ionisation of He	
Disappearance of He	30000°	10^{-5}	He completely ionised	Oa
Luminescence of H begins at	4500°	1 Atm.	Appearance of (2, p) orbit	
Luminescence of He begins at	12000°	"	" (2,p)	Ao
Maximum Luminescence of H	12000°	"		Ao
Maximum Luminescence of He	17000°	"		B _{II} A

The table contains the results of the application of the above formulæ to problems of stellar spectra. A physical basis is thus provided for the Harvard classification of stars according to the nature of their spectra. Column 5 shows the stellar-class at which the phenomena described under column 1 take place. This has been compiled from the Harvard Annals. The temperature under column 2 has been calculated from the formulæ given in the papers.

The conclusion is therefore made "The continuous variation of stellar spectral types, as observed by the Harvard Astrophysicists, can mainly be ascribed to the varying value of the temperature of emission of the stellar atmospheres".

We can now furnish a complete scheme of the train of physical phenomena which we come across when the temperature is gradually enhanced.

Phase	Phenomena	Example	Temp.
Solid	Liquefaction	Ice	
Liquid			
Gas	Vaporization	Water	
Gas (molecules of the constituents)			
Gas (molecules of the constituents)	Decomposition attended with the emission of H_2O -spectrum	Steam	
Gas (Atoms with (1, s) orbits)			
Gas (Atoms with (1, s) orbits)	Atomisation (Emission of the molecular Spectrum)	$H, O,$	
Gas (Atoms with (2, p) orbits)			
Gas (Atoms with (3, d) orbits)	Emission of (1, s) — (m, p) lines.		
Gas (Atoms with (3, d) orbits)			
Gas (Atoms with (3, d) orbits)	Emission of (2, p) — (m, d) lines		
Gas (Atoms with (3, d) orbits)			
Gas (Positively charged atom and the electron).	Ionisation (First Step)	H^+, e	
Gas (Atom with 2 plus charges & electron)			
Gas (Atom with 2 plus charges & electron)	Ionisation (Second Step)	Ca^+, e	
Gas (Atom with 2 plus charges & electron)			

etc. till in the interior of stars, the whole mass consists of positive nuclei, and electrons.

The theory probably also provides us with the long-sought for source of stellar energy. It is well-known that neither the energy of gravitational contraction nor the energy of radioactive disintegration suffice for this purpose. All observational data point out that the source is of the nature of latent heat, and it is only one step to conclude this heat is provided when, owing to a fall of temperature, a fraction of ionised atoms combines with electrons producing the neutral atom, or the ionised atom with one plus charge less, with the liberation of the latent heat of ionisation. The general trend of this source of heat will be to retard the progress of cooling, and it can come to action only at about 4000° .

NAME INDEX

- Abbot 91, 99
 Abelson 287, 290, 291, 292
 Abraham 11, 13, 230
 Acharya 236, 237
 Adams 52, 68, 76, 327
 Aiyyar, Nagaraja 296
 Allen 381
 Alvarez 286, 330, 337
 Ampere 23
 Anderson 208, 209, 212, 293, 296, 297, 298
 Angerer 243, 244
 Appleton, E. V 216, 249, 250, 251, 254, 256, 269, 270, 275, 276, 278, 281, 315, 316, 354, 368, 369, 371, 377, 378, 386, 389, 390
 Aschkinass 91
 Atkinson 210
 Avogadro 40, 114

 Babcock, H. D 219, 296, 321, 326
 Babcock, H. W 219
 Bacher 231, 283, 285, 292, 329, 331
 Backus 346
 Bajpai 250, 281
 Balmer 22, 63, 65, 66, 67, 68, 78, 88, 89, 97, 98, 99, 100, 140, 218, 240
 Banerjee, B. K 319, 354, 368, 369, 376, 378, 385, 388, 389, 401
 Banerjee, B. M 403, 405
 Bar 192
 Barkas 331, 342
 Barratt 48
 Barthelot 14, 15
 Bartlett 283
 Bartoli 2, 6, 7, 21, 111
 Barton 283
 Basu, D 315, 353
 Basu, N 9
 Baxandall 85, 86
 Baxter 367
 Bayley 341
 Bazzoni 58, 66
 Beals 218
 Becker 100, 102, 113
 Beese 133
 Bergmann 48, 57, 66, 87
 Beringer 377, 378
 Berkner 250, 269
 Berman 367
 Bethe 233, 272, 283, 285, 286, 292, 300, 306, 321, 325, 329, 330, 331, 332, 336, 347, 350
 Betti 24
 Bevan 57, 62, 71, 105
 Bhagavantam 192
 Bhargava, S 95
 Bhattacharyya, D. K. 180
 Bhattacharyya, P. C. 301, 306
 Birge 233, 236, 258
 Biscoe, F 35, 41, 68, 77
 Bjerge 341
 Blackett 208, 212
 Bleakney 286

 Bloch 300
 Böggild 324
 Bohr, N 22, 37, 43, 55, 58, 62, 70, 83, 86, 87, 89, 140, 141, 142, 149, 150, 157, 158, 159, 177, 202, 206, 207, 208, 212, 213, 231, 232, 284, 290, 300, 306, 324, 325, 326, 332
 Boltzmann 14, 15, 83, 84, 88, 106, 113, 132, 182
 Booker 249, 278, 279, 389, 396
 Born, M. 25, 26, 140, 234, 243, 244, 247, 309
 Börnstein 198
 Bose, D. M. 185, 193, 196, 235
 Bose, S. N 14, 20, 32, 55, 58, 102, 111, 113, 182, 183, 184, 278, 280, 281
 Bowen 131, 133, 140, 152, 153, 154, 155, 158, 159, 169, 170, 171, 172, 173, 174, 184, 319, 326, 385
 Bower 341
 Bradt 337, 401
 Bragg 59, 152
 Brandt 97
 Breit 333, 334
 Brill 255
 Brillouin, L 183, 184
 Brinkmann 302, 304, 308, 309, 311, 313, 320, 326
 Broadway 236, 237
 Brons 223
 Brooksbank 47
 Broström 341
 Brown, H 284
 Broxon 381
 Brunner, W. 386
 Brunt, D 34, 35
 Buisson 3, 37, 60, 255
 Bumbauch 295, 381, 386
 Bunsen 56
 Burcham 341
 Butler 85, 86

 Cabannes 217, 220, 224, 242
 Cailletet 15
 Campbell, N. R 22
 Cannon, A. J. 59
 Cario 236, 237, 241
 Carnot 111
 Catalan 59, 85, 140
 Cayley 316, 317
 Chadwick 206, 209, 210, 212, 301, 302
 Champion 336
 Chapman, S 215, 216, 241, 254, 257, 269, 270, 271, 272, 273, 275, 276, 277, 282, 317, 355, 380, 382, 383, 386
 Cillie 295
 Clausius 5, 14, 18, 24, 28, 31
 Coblentz 91
 Collins 242, 256, 261, 262
 Compton 92
 Condon 210, 211, 213, 220, 237, 238, 259, 272, 306
 Copson 311
 Cornog 286
 Corson 324
 Cortie 51
 Coster 149, 214, 223

- Cosyns 215
 Crane 341
 Crehore 17
 Cripps 15
 Crommelin 15
 Crookes 6
 Cunningham 32
 Curie 208, 209, 212, 329, 347, 349, 353
 Curran 344
 Curtis 335

 Dancoff 337
 Darwin 87, 88, 89, 90, 101, 102, 111, 185, 316, 319, 368
 Das 346
 Davies 54, 62
 Debije 37
 De Broglie 140, 157, 229, 353
 de Bruin 155, 171
 de Kronig 206
 De Mairan 6
 Deb, S. C. 195, 198
 Debye 278
 Dejardin 254, 256, 257
 del Rosario 214
 Dellinger 276
 Delsasso 286, 335
 Dempster 330
 Deslandres 223, 228
 Deutsch 342, 344, 346
 Dhar, N. R. 105, 194
 Dickey 377, 378
 Dieterici 14
 Dietzius 91
 Dingle 155, 171
 Dirac 140, 157, 158, 165, 182, 183, 187, 208, 209, 210, 231, 232, 234, 310, 327, 330, 388
 Dobbie 57
 Dobson 241, 242, 255, 323
 Domcke 98
 Doppler 3, 77
 Doran 337
 Dorgelo 139
 Drude 81, 89, 90
 Du Fay 6, 217, 219, 224
 Du Gramont 56, 63
 Dube 361
 Dubridge 286
 Duckworth 330
 Dunham, T 248
 Dutt 73
 Dutt, A. K. 195
 Dyson 294

 Eastermann 209, 234
 Eckersly 376
 Eddington 33, 36, 39, 44, 61, 78, 88, 91, 210, 232, 233, 407
 Edlen, B 201, 293, 306, 321, 322, 326
 Eggert, J 39, 40, 61, 69, 117, 407
 Eggerton, A. C. 69
 Ehrenfest 102, 108, 109, 113, 157, 177, 182
 Einstein 10, 14, 22, 25, 56, 62, 63, 115, 157, 177, 182, 183, 184
 Elliot 334, 342, 344, 346
 Ellis 206, 207, 212, 301, 302
 Ellsworth 367
 Elsasser 283

 Emden 36, 46, 64
 Enskog 102
 Epstein 389
 Eucken 116
 Euler 297
 Evans 66, 197, 198, 365, 366, 367
 Eve 58
 Evershed 36, 49, 51, 52, 296, 320

 Fabry 3, 4, 34, 37, 60, 255
 Fajans 193, 198
 Faraday 212, 244, 246
 Feenberg 331
 Fenyi 36
 Fermi 182, 183, 201, 231, 346
 Finney 365
 Fizeau 3
 Fleming, J. A. 328
 Flugge 306, 330, 344
 Foote 62, 112
 Forsterling 389
 Fowler 38, 46, 47, 48, 49, 50, 51, 59, 62, 64, 66, 67, 68, 73, 86, 87, 88, 89, 90, 95, 97, 98, 100, 101, 102, 106, 111, 112, 113, 116, 120, 128, 140, 153, 154, 169, 171, 173, 174, 211, 255, 308, 319
 Fowler, R. H. 113, 154, 210, 235, 319
 Fox 57
 Franck 40, 43, 44, 53, 62, 66, 70, 95, 96, 117, 185, 195, 196, 197, 220, 237, 238, 244, 259, 272, 407
 Fraunhofer 39, 45, 46, 47, 49, 77, 98, 99, 116, 176, 228, 259, 260, 295, 296, 297, 308
 Fredenhagen 79
 Freeman 169, 173
 Frish 192
 Fuchtbauer 112
 Fues 62

 Gamow 206, 209, 210, 211, 212, 213, 252, 283, 306, 321
 Gans 252
 Gapon 283
 Gaskugeln 64
 Gauss 18, 23, 24
 Gauzit 217, 219, 224
 Geiger 207
 Gentner 208, 212
 Geovanelli 386
 Gerlach 157, 192, 237, 356
 Ghosal, S. N. 347, 353
 Ghosh, J. C 44
 Ghosh, R. N 125
 Ghosh, S. K 68, 306
 Gibbs, W 102, 182, 184, 315, 317
 Gibson 53, 244
 Giebert 337, 338, 343, 352
 Gobau 249, 251
 Goldstein 46, 47, 62, 185
 Goodal 250
 Gotz 130, 221, 241, 242, 255
 Goubau 281, 282
 Goucher 54, 62
 Goudsmit 136, 137, 138, 140, 144, 155, 157, 199, 234
 Grahame 342
 Grassmann 24
 Graves 330
 Gray 15, 208, 212
 Greenstein 354, 355
 Gregoire 284, 286, 289

- Griffiths 196
 Groot 91
 Grotian 48, 50, 293, 295, 297, 298, 306, 322
 Guggenheimer 283
 Guha, U. C 376, 378, 385, 388, 389, 401, 403
 Guldberg 113
 Gunther, P 89, 117
 Gurney 210, 211, 213
 Hadamard 278
 Hagen 91
 Hahn 290, 291, 324
 Hale 51, 378, 379, 380, 381
 Hall 184
 Hamada 236, 237
 Hamilton 107, 111, 316, 317
 Hankel 311
 Hanle 192
 Hansen, G 187
 Harang, Leiv 250, 315, 354
 Harkins, W. D 283
 Harrison 402
 Hartdke 97
 Hartree 154, 249, 278, 315, 316, 368, 378, 389
 Haxby 332, 333, 334, 335
 Heaviside 215
 Heisenberg 125, 126, 127, 132, 140, 145, 157, 158, 159, 165, 186, 187, 189, 231, 244, 283, 297
 Heitler 244
 Helmholtz 243, 247
 Hemmendinger 342
 Hemsalech 71
 Henderson 215, 302, 307, 308, 320, 335, 336, 337, 342
 Henyey 354, 355
 Herglotz 29
 Hertz 40, 44, 53, 62, 70, 117, 136, 158, 173, 202, 407
 Hertzprung 33
 Herweg 79
 Herzberg 217, 218, 221, 236, 260, 261
 Herzfeld 184, 273
 Hevesy 149, 284
 Hewson 328
 Hey 377, 378, 386
 Hibdon 334, 338, 340, 342, 346
 Hittorf 78, 79, 81, 94
 Hoff 113
 Hoffmann 193
 Holt 342
 Hopfield 116, 154, 221, 256, 258, 259
 Horowitz 324
 Horton 54
 Houtermans 210
 Huber 336
 Huggins 52, 87
 Hulburt, E. O 255, 276, 277
 Hull 6, 7, 8
 Hulme 214
 Hulst 381
 Hund 120, 121, 125, 126, 127, 129, 132, 134, 137, 140, 142, 153, 154, 155, 158, 159, 173, 178
 Hupfeld 208
 Hylleras 201, 202, 204, 309
 Infeld 234
 Itoh 344
 Ivanenko 283
 Jacobi 37
 Jacobsen 302, 304, 308, 320
 Jackson 236, 237
 Jansen 47
 Jeans 5, 61, 83, 88, 111, 210
 Jewell 387
 Jog, D. S 171
 Johnson, M. C 100
 Johnson, R. C 105
 Joliot 208, 209, 212, 329, 349
 Jordan 140, 186, 187, 189
 Jouaust, R 250
 Joy 327
 Judson 215, 250
 Julius 36
 Kamen 337, 341
 Kaplan 223, 224, 236, 237, 242, 258, 259
 Kastler 192
 Kaufmann 230
 Kayser 46, 58, 135, 140
 Keenan 354, 355
 Keesom 15
 Keevil 363, 366, 367
 Kellner 158, 201
 Kelvin 362
 Kemmer 353
 Kennedy 290
 Kennelly 215
 Kepler 6
 Kichlu 121, 123, 124, 152, 155, 159, 176, 178, 236, 237
 Kiess 101, 116
 King 42, 44, 53, 71, 85, 92, 93, 334
 Kirby 215, 250
 Kirchhoff 34, 45, 56, 57, 140
 Klein 95, 96
 Klement 76
 Klemperer 353
 Klotz 21
 Klutke 76
 Knipp 300, 324, 333
 Koch 174
 Kohlschütter 68, 76
 Kohn 105
 Konen 135, 140
 Konopinski 330, 332, 333, 334, 337, 341, 344
 Kossel 39, 86, 140, 151
 Kothari, D. S 213, 232, 235
 Kramers 271, 272, 302, 304, 308, 309, 311, 313, 320, 326
 Kreussler 261
 Krishnan 177
 Krüger 341, 342, 351
 Kuhlenkampf 207
 Kuhn 195, 196, 244, 273
 Kundu, D 293, 294, 306, 326
 Kunze 209
 Kurbatov 335, 340, 342
 Kurie 286, 337, 338, 344
 Ladenburg 22, 42, 63, 193, 241, 242, 254, 259, 272
 Lamb 300, 324
 Landé 83, 125, 126, 135, 137, 140, 143, 144, 146
 Landolt 198
 Lane 361, 367
 Lang 184
 Langmuir 43, 47, 48, 49, 83, 91,

- Langsdorff 292
 Lark 324
 Larmor 21
 Larsen 366
 Laski 49
 Lassen 278
 Laue 69, 210
 Lawson 335, 342
 Lebedew 7, 8, 21, 33
 Lederley, E 244
 Lee 342
 Lehmann 300
 Leibnitz 340, 341, 351
 Leifson 197
 Lenard 270, 277
 Levi 284
 Lewis 15, 92, 235
 Libby 289, 342
 Lichtblau 289
 Lienard 16, 29, 31
 Lindemann 52, 61, 323
 Lindh 202, 203
 Liouville 107
 Lippich 3
 Livingood 290, 329, 335, 337
 Livingstone 300, 324
 Lockyer 38, 59, 60, 62, 85, 86, 140
 Lorensen 38, 62
 Lorentz 1, 10, 11, 12, 13, 14, 17, 19, 25, 28, 30, 31, 230, 231
 Loria 22, 42, 63
 Loring 83
 Love 5
 Loving 49
 Lummer 91, 105, 198
 Lunt 47, 51, 52, 86
 Lyman 43, 65, 67, 88, 97, 218, 219, 221, 242, 259, 261
 Lyot 298, 321, 324, 327

 Mackenran 407
 Macmillan 341
 Magnan 340
 Magnusson 214
 Mahadevan 361
 Maier 340, 341, 351
 Mainsmith 140, 142, 156, 159
 Mallik, D. N. 1, 2, 23, 32
 Mann 346
 Maris 255, 276
 Martyn 378, 385, 386
 Mathias 15
 Mathur, K. B 250, 254, 276, 278, 316, 368, 369, 371
 Mathur, L. S 228, 258
 Mattauch 289, 330, 344
 Maxwell 1, 2, 4, 6, 7, 11, 13, 21, 24, 94, 102, 315
 Mayer 243, 244, 247
 Mazumdar, K 95, 130, 139, 172, 176, 184
 Mazumdar, R. C 272, 277
 McCready 355, 377, 378
 Mckeown 196
 McLennan 40, 43, 53, 62, 79, 81, 89, 94, 153, 171
 Mecke 261
 Meetham 221, 241, 255
 Meggers 62, 73, 116
 Meisenheimer 193
 Meissner 155

 Meitner 208, 344
 Melnikov 296, 308, 320
 Menzel, D. B. 293, 295, 319, 325, 402
 Merrill 248, 326
 Merton, T. R 105
 Michelson 3, 4
 Mihul 169, 173
 Millikan 22, 83, 131, 133, 140, 152, 153, 158, 159, 169, 170, 172, 173
 Millmann 297
 Milne, E. A 82, 90, 91, 98, 99, 101, 102, 105, 112, 113, 115, 175, 262, 269, 271, 295, 319
 Minkowski 10, 11, 13, 15, 16, 17, 19, 25, 27, 31
 Minnaert 218, 219, 293, 295, 296, 298, 308, 320, 322
 Mitchel 35, 38, 39, 44, 46, 48, 77, 89, 176, 218, 402
 Mitchell, S. A 295
 Mitra, S. K 215, 249, 251, 254, 263
 Mohanti, H. B 195, 198
 Mohler 62, 112
 Möller 330
 Moltchanoff 241
 Moore 297, 322, 326, 381
 Mott 214
 Mukerji, B 195
 Mukherjee 329, 349
 Mulders 255
 Müller 196, 243, 244
 Mulliken 204, 243, 256, 260, 261

 Nag, N. C 361
 Naismith 216, 250, 270
 Natanson 88
 Neddermeyer 208, 209, 212
 Nelson 335
 Nelthorpe 62
 Nernst 44, 54, 61, 69, 81, 87, 89, 92, 108, 109, 113, 406, 407
 Neumann 24
 Newall 50, 51, 52
 Newson 286
 Newton 6
 Nichols 6, 7, 8
 Nicholson 3, 21, 23, 37, 88, 89, 379, 383
 Nicolet 379
 Nielson 335
 Nier 286, 287, 347, 362, 363, 365, 366, 367
 Noyes, A. A 89
 Nuttall 207

 Ochialini 208, 212
 Ogle 341, 342, 351
 Ohm 89
 Okubo 236, 237
 Oldenberg 244
 Olmsted 51
 Onnes, K 15
 Oppenheimer 208, 210, 308, 320
 Ornstein 139
 Ostwald, W 102
 Otto Laporte 126, 127

 Paneth 258, 366
 Pannekoek, A 269, 270, 271, 272, 274, 276, 295, 296, 308, 319, 320
 Pant 250, 281
 Parhe 63
 Parker 94

- Paschen 40, 47, 55, 58, 62, 63, 65, 134, 136, 137, 138, 140, 155, 159,
 187, 218, 356
 Pasternack 306
 Paterson 15
 Pauli 119, 122, 125, 126, 127, 128, 130, 131, 132, 133, 140, 142, 143, 157,
 159, 184, 193, 199
 Pauling 199
 Pawsey 355, 377, 378
 Payne, C 116, 319, 355, 377, 378
 Pease 52
 Pedersen 216, 317
 Perepelkin 296, 308, 320
 Perlov 324
 Perot 3, 4, 37
 Peters 401, 402
 Petit 255
 Pfund 184
 Piccard 215
 Pickering 59, 60, 66, 68
 Pirani 98
 Planck 2, 50, 54, 56, 62, 63, 106, 107, 108, 109, 110, 111, 182, 207
 Plaskett, H. H 255, 262
 Plesset 208, 337
 Poincaré 26
 Pollard 347
 Pool 334, 338, 340, 342, 346
 Popow 130
 Porter, A.W 9
 Poynting 17, 21
 Present 324
 Price 242, 256, 261, 262
 Pring 94
 Pringsheim 23, 45, 47, 49, 51, 53, 70, 104, 177
 Prins 214
 Pryce 234

 Rabi 355, 356, 357
 Rai, R. N 235, 250, 276, 278, 281, 316, 368, 369, 371, 389
 Rakshit 254
 Raman, C. V 9, 177, 192, 198
 Rankine 58, 59
 Ranzi 250
 Ratcliffe 250, 251
 Rau, 43
 Rawer 389
 Ray, B. B 121, 128, 129, 156, 159, 199
 Rayleigh 3, 4, 37, 95, 97, 98, 225, 237, 250, 252, 295, 322
 Regener 221, 241, 255
 Reiche 43, 62
 Rentschler 54
 Richardson 58, 66, 78, 79, 205, 338, 381
 Ridenour 335, 337
 Riemann 24
 Ritz 38, 140
 Robinowicz 55, 192
 Rogers 205
 Rognley 62
 Rollefson 195, 196
 Rontgen 89
 Rosseland 95, 96, 218, 241, 272, 295, 298, 327, 380
 Rossi 51
 Rowland 45, 50, 140, 175
 Roy, R 403, 405, 406
 Rubens 91, 341
 Runge 48, 50, 116, 140, 220, 221, 242, 243, 260, 261

 Russel, H. N 33, 44, 59, 60, 68, 76, 82, 86, 87, 99, 101, 102, 103, 112,
 125, 127, 130, 134, 135, 136, 138, 140, 143, 145, 150, 151, 184,
 205, 255, 262, 293, 296, 298, 300, 319, 321, 381
 Rutherford 58, 86, 206, 212, 301, 302, 304, 306, 307, 308, 320
 Rydbeck 371, 389, 391, 401
 Rydberg 38, 39, 54, 55, 58, 62, 130, 131, 132, 133, 135, 136, 138, 139,
 140, 144, 150, 151, 154, 155, 159, 256, 261
 Ryle 378, 386

 Sackur 50, 69, 108, 113, 407
 Saha, A. K 337, 341, 346, 347, 349, 352, 353
 Saha, N. K 228
 Sakata 330
 Sargent 207
 Saunders 100, 127, 130, 134, 135, 136, 138, 143, 145, 150, 151, 205
 Sawyer 133
 Schafer 250
 Scheiner 68, 84, 91
 Scherr 341
 Schillinger 62
 Schönrock 3, 4, 37
 Schrödinger 140, 157, 158, 210, 234
 Schulz 247
 Schumann 62, 169, 170, 175, 220, 221, 237, 242, 243, 260, 261
 Schuster, A 215, 317
 Schwarzschild 21, 33, 34, 35, 41, 91, 295, 322, 381
 Scott 355, 377, 378, 395
 Seaborg 290, 291, 329, 333, 335, 337, 341, 349
 Sengupta, P. K 228, 258
 Shapley 262, 328
 Sharma 243
 Shenstone 184
 Shortley 306
 Siegbahn 123, 148
 Sirkar 329, 349
 Skobelzyn 208, 211
 Slipher 217, 228, 255, 256, 259, 276
 Smekal 177
 Smits 101, 104, 113
 Snell 286
 Sommer 121, 217, 220, 221, 224, 255, 259, 341
 Sommerfeld 16, 19, 25, 26, 29, 37, 39, 54, 55, 56, 58, 62, 70, 86, 120,
 126, 127, 139, 140, 141, 143, 144, 146, 151, 185, 186, 187, 192, 202,
 231, 232, 234, 320
 Sponer 236, 259
 Srivastava 218, 244
 Stark 83, 97
 Stefan 24, 35
 Sterm 234
 Stern 84, 157, 192, 209, 237, 356
 Stevens 261
 Stewart, B 215
 Stewart, J. Q 90, 91, 112
 Stimson 62
 Stirling 107, 114
 Stobbe 304
 Stoner 118, 130, 137, 140, 142, 143, 156, 159, 184, 193, 202
 Störmer 254, 256, 328
 Strasseman 324
 Stratton 316, 369
 Strutt 94, 95, 97, 235, 255
 Struve 319, 327
 Stueckelberg 222
 Sugiura 158
 Sur, N. K 117, 124, 153, 174, 182, 235

- Sutton, P. P 244
Swaminathan 361
Swann 215
Swings 321, 327
Swirles 214
Syam, P 215
Szilard 290, 324

Takens 214
Tamm 210, 232
Tandon, A. N 245
Tarrant 208, 212
Taylor 214, 249, 281, 282
Teller 300, 324
Tetrode 69, 407
Thackeray 293
Thibaud 201, 214
Thomas 273, 303, 308
Thompson, J. H 81, 230
Thomsen 198
Thomson, J. J 1, 14, 18, 19, 24, 63, 71, 79, 81, 88, 89, 90, 94, 113, 230, 300, 302, 320, 342
Thornton 324
Tiede 98
Toshniwal, G. R 228, 254, 315, 354
Townsend 337
Trkal 108, 109, 182
Turner 329, 342
Tyler 346

Uhlenbeck 140, 144, 157, 234
Unsold 144, 158, 185, 186, 187, 295, 319, 380
Urey 100
Urry 363

Van der Waals 14, 183, 184
Van Voorhis 337
Van't Hoff 113
Vegard 217, 223, 224, 236, 242, 258, 259
Verma, J. K. D 403, 405, 406
Vinti 272, 273
Vogel 52
Vonberg 378, 386

Waage 113
Wadia, D. N 365, 368

Waldemeier 298, 324
Walke 324, 337, 340, 342, 344
Warburg 221
Wartenburg 247
Watanabe 340
Watase 334, 339, 342, 344
Weber 18, 24
Weimer 334
Weizsacker 330, 331, 332, 347, 350
Wells 250
Wentzel 130, 214
Westphal, W 76
Weyl 185
Wheeler 284, 290, 300, 306, 324, 326, 332
White 184, 250, 251, 340
Whytlaw 15
Widdowson 336
Wiechert 16, 29, 31
Wien 91, 97
Wigner 158, 331
Wildt 381
Wilkins 83
Williams, E. J. R 295, 303
Wilsing 68, 91, 99
Wilson, H. A 81, 89, 208, 210, 388
Wolf 273
Wolff 62
Woltjer 115, 269
Wood 57, 62, 89, 96, 98, 101, 105, 112
Wood, R. W 21, 71, 177, 178
Woolley 294
Wrede 236, 237
Wright 86, 100
Wulf 256

Yasaki 340
Yukawa 330

Zacharias 342
Zanstra 227, 228, 319
Zeeman 130, 134, 135, 136, 137, 140, 141, 146, 192
Zeneck 251
Zinn 290, 324
Zöllner 6, 7

